

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

JANUARY, 1937.

Direct introduction of deuterium into aliphatic systems. I. Hydrogen exchange between sulphuric acid and paraffinoid hydrocarbons. C. K. INGOLD, C. G. RAISIN, and C. L. WILSON (J.C.S., 1936, 1643—1645).—In accordance with the theory that deuteration with DHSO_4 is an electrophilic exchange, and should occur preferentially at *tert.* C atoms, the ease of H exchange between DHSO_4 and paraffins is found to follow the series, methyl-*cyclohexane* > *n*-hexane > *n*-heptane > *cyclohexane*.

J. D. R.

Deuterium content of the hydrocarbons of light petroleum from different sources. A. MAILLARD (Compt. rend., 1936, 203, 804—806; cf. A., 1935, 1099).—Measurements of f.p. and n_D^{20} on the H_2O - D_2O mixture, appropriately conc., obtained when light petroleum (I) is burnt give a measure of the D_2O content, which is different for different samples of (I).

J. L. D.

Pyrolysis of propane and the butanes. G. EGLOFF, C. L. THOMAS, and C. B. LINN (Ind. Eng. Chem., 1936, 28, 1283—1294; cf. A., 1930, 1268).—Pyrolysis under varying conditions of temp. (600—700°), pressure (1 and 7 kg. per sq. cm.), and time (0—2 min.) of C_3H_8 , *n*- and *iso*- C_4H_{10} has been studied in detail. C_3H_8 yields H_2 , CH_4 , C_2H_4 , C_3H_6 , and C_3H_8 ; *n*- C_4H_{10} , as C_3H_8 with C_3H_8 and *n*- C_4H_8 ; *iso*- C_4H_{10} , as *n*- C_4H_{10} with *iso*- C_4H_8 . The concn. of olefines in the final gas increases with time to a max. and then decreases; when two or more olefines are produced the max. are not necessarily coincident. Increasing pressure decreases the amount of olefines produced, but this is compensated by an increasing reaction rate. Rise of temp. increases concn. of olefines, which are produced, under stated optimum conditions, in yields of 30—40%.

R. F. P.

Preparation of diethyltetradecane. S. LANDA and M. HABADA (Coll. Czech. Chem. Comm., 1936, 8, 473—476).— Et_2 sebacate and MgEtBr give γ -diethyltetradeca- γ -diol, m.p. 59°, slowly dehydrated by ZnCl_2 at 115° to γ -diethyl- $\Delta^{\beta\mu}$ -tetradecadiene, b.p. 168°/16 mm., which with KMnO_4 gives tetradeca- γ -dione, m.p. 79°, and with H_2 -Ni at >180°/112 atm. yields γ -diethyltetradecane, b.p. 151°/2 mm., m.p. about -30°.

R. S. C.

Propylene polymerisation under high pressure and temperature with and without phosphoric acid. V. N. IPATIEV and H. PINES (Ind. Eng. Chem., 1936, 28, 684—686).—The approx. composition of the products of the thermal polymerisation of propylene at 375° for 12 hr. (pressure fell from 214 to

54 kg. per sq. cm.), and catalytic (H_3PO_4) polymerisation at 330° for 8 hr. (pressure fell from 102 to 42 kg. per sq. cm.) is, respectively: paraffins, 8, 15; olefines, 26, 63; cycloparaffins, 44, 10; cycloolefines, 22, 6; aromatic, 0, 6%. The catalytic polymerisation is more rapid than the thermal.

P. G. C.

Hydropolymerisation, a new type of polymerisation of ethylenic hydrocarbons under the influence of sulphuric acid. S. S. NAMETKIN and L. N. ABAKUMOVSKAJA (J. Gen. Chem. Russ., 1936, 6, 1166—1176).—Ethylenic hydrocarbons undergo partial dehydrogenation in conc. H_2SO_4 , with simultaneous formation of saturated polymerides, termed hydropolymerides. Thus isobutylene yields a mixture of the hydropolymerides, C_8H_{18} , b.p. 106—108°/770 mm., $\text{C}_{12}\text{H}_{26}$, b.p. 177—179°/748 mm., $\text{C}_{16}\text{H}_{34}$, b.p. 242—246°/746 mm. (contains 15% of $\text{C}_{16}\text{H}_{32}$), $\text{C}_{20}\text{H}_{42}$, b.p. 150—153°/10 mm. (contains 35.2% of $\text{C}_{20}\text{H}_{40}$), $\text{C}_{24}\text{H}_{50}$, b.p. 153—154°/2 mm. (contains 42.3% of $\text{C}_{24}\text{H}_{48}$), and a complex mixture of higher saturated and unsaturated polymerides. Similarly, technical amylene, b.p. 35—37°, yields $\text{C}_{10}\text{H}_{22}$, b.p. 155—165°, $\text{C}_{15}\text{H}_{32}$, b.p. 240—243°, $\text{C}_{20}\text{H}_{42}$, b.p. 150—160°/10 mm., $\text{C}_{25}\text{H}_{52}$, b.p. 158—165°/2 mm., and $\text{C}_{30}\text{H}_{62}$, b.p. 185—195°/2 mm., whilst $\text{CH}_2\text{:CHPr}^\beta$ affords $\text{C}_{10}\text{H}_{22}$, b.p. 150—151°/739 mm., $\text{C}_{15}\text{H}_{32}$, b.p. 240—245°/733 mm., and $\text{C}_{20}\text{H}_{42}$, b.p. 130—135°/2 mm., and octene gives $\text{C}_{16}\text{H}_{34}$, b.p. 130—140°/15 mm. (containing 19% of $\text{C}_{16}\text{H}_{32}$), and $\text{C}_{24}\text{H}_{50}$ (impure).

R. T.

Catalytic isomerisation of diallyl and eugenol. R. J. LEVINA (J. Gen. Chem. Russ., 1936, 6, 1092—1095).—Diallyl and eugenol are converted respectively into dipropenyl and isoeugenol when passed over Pd- or Pt-asbestos at 200—300°.

R. T.

Hydrolysis of alkyl halides. I. S. C. J. OLIVIER [with (MILES.) M. BOSMAN and M. K. BOUWMAN] (Rec. trav. chim., 1936, 55, 1027—1035).—The following preps. are described. *n*- $\text{C}_5\text{H}_{11}\text{OH}$ (purified by way of the *p*-hydroxybenzoate, m.p. 35.8—36.7°) and red P-HBr (saturated at 0°) at 100° give *n*- $\text{C}_5\text{H}_{11}\text{Br}$, b.p. 128.7—129.4°/757 mm. $\text{CH}_3\text{AcCO}_2\text{Et}$ gives $\text{CHPr}^\alpha\text{AcCO}_2\text{Et}$ (60%), b.p. 208—216°, and thence *n*-hexan- β -one (50%), b.p. 126.6—127.2°/749 mm., (Na-EtOH) *n*-hexan- β -ol, b.p. 139.8—140.8°/776 mm., and *n*- $\text{C}_6\text{H}_{13}\text{Br}$, b.p. 144—144.5°/767 mm. $\text{CHMe}(\text{CO}_2\text{Et})_2$ gives successively impure $\text{CMePr}^\alpha(\text{CO}_2\text{Et})_2$, $\text{CMePr}^\alpha(\text{CO}_2\text{H})_2$, pure α -methyl-*n*-valeric acid, b.p. 195—196°, Et α -methyl-*n*-valerate, b.p. 153.5—154°/758 mm., β -methyl-*n*-amyl alcohol, b.p. 147.5—148°/766.4 mm.,

and bromide, b.p. 142—145° (slight decomp.)/748.3 mm. (very readily hydrolysed by H_2O , probably by preliminary isomerisation to $\text{CMe}_2\text{Pr}^a\text{Br}$). *sec.*-BuI gives successively Et_2 *sec.*-butylmalonate (88%), the corresponding acid (42%), β -methyl-*n*-valeric acid (75%), b.p. 197.5—198.4°/760.8 mm., and its Et ester, b.p. 158.5—159°/756.3 mm., γ -methyl-*n*-amyl alcohol (65%), b.p. 152.3—153°/765 mm., and bromide, b.p. 148.6—149.4°/766.3 mm. BuI gives successively $\text{CHBu}^a(\text{CO}_2\text{Et})_2$, b.p. 107.5—108°, γ -methyl-*n*-valeric acid, b.p. 199—200°/755.4 mm., and its Et ester, b.p. 159.5—160.5°/750.3 mm., δ -methyl-*n*-amyl alcohol, b.p. 151.5—152.5°/763.2 mm., and bromide, b.p. 147—148°/759 mm. $n\text{-C}_6\text{H}_{13}\cdot\text{OH}$ (purified by way of the *p*-hydroxybenzoate, m.p. 52.2—52.8°), b.p. 157—157.8°/760.2 mm., gives the bromide, b.p. 155.2—155.8°/759 mm., which with hot *N*-KOH gives slowly $\text{C}_6\text{H}_{13}\cdot\text{OH}$ and a little *di-n-heavy* ether, b.p. 228—229°/761.2 mm.; the chloride has b.p. 132—133°. The b.p. of the isomerides decreases as the substituent Me approaches the functional group. R. S. C.

Aliphatic chloro-derivatives. I. Chlorination of trimethylethylene. D. V. TISCHTSCHENKO (J. Gen. Chem. Russ., 1936, 6, 1116—1132).—The products of reaction of 1 mol. of Cl_2 with 1 mol. of $\text{CHMe}\cdot\text{CMe}_2$ (I) at -17° are: CMe_2EtCl (II), $\text{CHMeCl}\cdot\text{CMe}\cdot\text{CH}_2$ (III), α -chloro- β -methyl- Δ^a -butene (IV), b.p. 108—110°, $\text{CHMeCl}\cdot\text{CMe}_2\text{Cl}$ (V), $\alpha\gamma$ -dichloro- β -methylbutane (VI), b.p. 155°, $\alpha\beta\gamma$ -trichloro- β -methylbutane (VII), b.p. 73—74°/19 mm., $\beta\delta$ -dichloro- γ -chloromethylbutane (VIII), b.p. 79—81°/15 mm., and $\beta\gamma\delta$ -trichloro- γ -chloromethylbutane (IX), b.p. 102—103°/13 mm. On further chlorination, (II) yields a mixture of $\beta\gamma$ -trichloro- γ -methylbutane (X), m.p. 170°, and (V), (VII), and (IX). The process is supposed to consist of the reactions: (I) + $\text{Cl}_2 \rightarrow$ (V); (V) \rightarrow (III) + HCl; (I) + HCl \rightarrow (II); (III) + HCl \rightarrow (V) + (VI); (III) + $\text{Cl}_2 \rightarrow$ (VII); (VI) + $\text{Cl}_2 \rightarrow$ (VII) + (VIII); (VII) or (VIII) + $\text{Cl}_2 \rightarrow$ (IX); (V) + $\text{Cl}_2 \rightarrow$ (VII) + (IX) + (X); (III) \rightarrow (IV). (VI) and (VIII) are readily hydrolysed by aq. KOH to yield alcohols and tarry products, with elimination of HCl. Most of the remaining Cl-derivatives are either unattacked by aq. KOH, or yield unsaturated products; thus, (IX) gives $\text{CHCl}\cdot\text{C}(\text{CH}_2\text{Cl})\cdot\text{CHMeCl}$. When treated with quinoline at 150° the compounds behave differently; thus (V) does not react, (VI) gives isoprene in 10—15% yield, with traces of γ -chloro- β -methyl- Δ^a -butene (?) (XI), b.p. 106—108°, (VII) gives β -chloroisoprene (XII) in 30% yield, (VIII) affords tarry products, with elimination of HCl, (X) gives (XII) in 60% yield and (XI), and $\text{CH}_3\text{Cl}\cdot\text{CMe}\cdot\text{CMeCl}$ gives $\text{CHCl}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2$ (60% yield). α -Chloroisoprenes condense with maleic anhydride to yield HCl and homologues of dihydrophthalic acid. R. T.

Action of concentrated aqueous sodium hydroxide on aliphatic nitro-compounds. H. S. FRY and J. F. TREON (Rec. trav. chim., 1936, 55, 1007—1014).—With 3*N*-NaOH at 130—140° (10 hr.) MeNO_2 gives 0.35 mol. each of Na_2CO_3 and NH_3 (cf. A., 1933, 1271); with *N*-NaOH, however, it gives 0.12—0.13 mol. of NH_3 and about 0.24 mol. of CO_2 ,

probably owing to partial simultaneous reaction to methazonic acid and thence to CO_2 , HCN, and NH_2OH . With 5*N*-NaOH at 130—140° (6 hr.) $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NO}_2$ gives quantitatively $\text{Na}_2\text{CO}_3 + \text{NH}_3 + \text{N}_2\text{O} + \text{H}_2\text{O}$, by way of $\text{CO}_2\text{Na}\cdot\text{N}\cdot\text{NO}\cdot\text{ONa}$, and nitroguanidine gives quantitatively $\text{Na}_2\text{CO}_3 + 2\text{NH}_3 + \text{N}_2\text{O}$, by way of $\text{ONa}\cdot\text{C}(\text{NH})\cdot\text{N}\cdot\text{NO}\cdot\text{ONa}$ and thence $\text{NH}\cdot\text{C}(\text{ONa})_2 + \text{N}_2\text{O}$; nitrobarbituric acid gives (25 hr.; 90% in Cu, 47% in Pyrex flasks) $4\text{Na}_2\text{CO}_3 + 3\text{NH}_3 + \text{H}_2\text{O}$, by way of MeNO_2 .

R. S. C.

Photochemical decomposition of nitromethane and nitroethane.—See A., I, 39.

Determination of isopropyl alcohol. H. KEMAL (Z. anal. Chem., 1936, 107, 33—34).—Aq. Pr^aOH is treated with cold $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$. After 24 hr., the solution is made alkaline with *N*-KOH, and COMe_2 formed is titrated with 0.1*N*-I. J. S. A.

Rotatory dispersion of configuratively related aliphatic carbinols. P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1936, 116, 209—219).—The rotatory dispersions of carbinols of the general type $\text{CH}_3\cdot[\text{CH}_2]_l\cdot\text{CH}([\text{CH}_2]_m\cdot\text{Me})\cdot[\text{CH}_2]_n\cdot\text{OH}$ are studied and discussed for the cases in parentheses, and the vals. of $[M]_{\text{max}}^{25}$ for various λ are tabulated for the following carbinols: *d*- $\text{CHMeEt}\cdot\text{OH}$ and *l*- $\text{CHPr}^a\text{Bu}^a\cdot\text{OH}$ in the homogeneous state and *l*- $\text{CHPr}^a\text{Bu}^a\cdot\text{OH}$ in Et_2O ($l = 0$ or 2, $m = 0$, $n = 1$ or 3); *l*- $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{OH}$ and *l*- $\text{CHMePr}^a\cdot\text{CH}_2\cdot\text{OH}$ ($l = 0$ or 1, $m = 1$, $n = 1, 2$, or 3); *d*- $\text{CHETPr}^a\cdot\text{CH}_2\cdot\text{OH}$, *d*- $\text{CHETBu}^a\cdot\text{CH}_2\cdot\text{OH}$, *d*- $\text{CHMeEt}\cdot[\text{CH}_2]_2\cdot\text{OH}$, *d*- $\text{CHMeEt}\cdot[\text{CH}_2]_3\cdot\text{OH}$, and *l*- $\text{CHET}(\text{CH}_2\text{Bu}^a)\cdot[\text{CH}_2]_2\cdot\text{OH}$ in the homogeneous state and *l*- $\text{CHMePr}^a\cdot[\text{CH}_2]_2\cdot\text{OH}$ in heptane ($l = 0$ or 1, $m = 2$ or 3, $n = 1$ or 2). All dispersions are represented by a single-term Drude formula. The dispersion curves of all *sec.*-carbinols are anomalous and the partial rotation of the first active band is of opposite sign to the observed rotation. Changes in direction of the individual rotatory components produced by progressive increase in *m* have been deduced. J. W. B.

Action of magnesium diethyl on methyl derivatives of ethylene oxide. F. H. NORTON and H. B. HASS (J. Amer. Chem. Soc., 1936, 58, 2147—2150).—No rearrangement occurs when the various oxides studied are treated with MgEt_2 ; the ease of fission of the C-O linking is primary > *sec.* > *tert.* With MgEtBr , rearrangement occurs and different alcohols are generally produced. Thus with MgEt_2 , $\alpha\beta$ -oxido-propane gives pentan- β -ol (23%) (also obtained in 11.7% yield, together with probably some pentan- γ -ol, using MgEtBr); $\alpha\beta$ -oxido- β -methylpropane (I) affords β -methylpentan- β -ol (27.5%); *cis*- (II), b.p. 58—59°/745 mm., and *trans*- (III), b.p. 52—53°/741 mm., $\beta\gamma$ -oxidobutane yield mixtures, b.p. 75.4—75.8°/70 mm. (61%) and 73—74°/70 mm. (21.8%), respectively, of γ -methylpentan- β -ols; $\beta\gamma$ -oxido- β -methylbutane (IV) furnishes 21% of $\beta\gamma$ -dimethylpentan- β -ol, b.p. 71—73°/50 mm., 139.7°/744 mm. (also prepared from *sec.*-BuMgBr and COMe_2); $\beta\gamma$ -oxido- $\beta\gamma$ -dimethylbutane (V), b.p. 90.2—91.4°/753 mm., gives $\beta\gamma\gamma$ -trimethylpentan- β -ol (34.6%). With MgEtBr , (I) affords β -methylpentan- γ -ol (21%); (II) and (III) yield γ -methylpentan- γ -ol, b.p. 62.6—

64.6°/70 mm. (17.5%) and 63.7—64.9°/70 mm. (49%), respectively; (IV) furnishes $\beta\gamma$ -dimethylpentan- γ -ol (50%); (V) gives $\beta\beta\gamma$ -trimethylpentan- γ -ol (38%). All the alcohols are also synthesised (Grignard methods); numerous physical data are given. (II) and (III) are prepared from γ -chlorobutan- β -ol, b.p. 76—79°/100 mm. (from *cis* + *trans*- Δ^2 -butene and HOCl) and solid KOH, and are separated by fractionation. (IV) is similarly obtained from β -methyl- Δ^2 -butene, whilst (V) is prepared from $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$. H. B.

Reaction of $\beta\gamma$ -oxidobutane with the Grignard reagent. D. L. COTTLE and L. S. POWELL (J. Amer. Chem. Soc., 1936, 58, 2267—2272).— Δ^2 -Butene and $\text{Br}\cdot\text{H}_2\text{O}$ give crude γ -bromobutan- β -ol (I), converted by aq. NaOH into $\beta\gamma$ -oxidobutane (II), b.p. 55—59°, which with 48% HBr at 0—2° affords pure (I), b.p. 46—50°/8 mm. (I) and MgEtBr (2 mols.) give 26% of (?) γ -methylpentan- γ -ol, some COMeEt, and a little of (probably) an octenone [*semicarbazone*, m.p. 250.5—251.5° (corr.) (decomp.)]; γ -methylpentan- β -ol is not produced. In agreement with Bartlett and Berry's views (A., 1935, 208), (II) with MgMe_2 and MgEt_2 affords γ -methylbutan- β -ol (35%) (*phenylcarbamate*, m.p. 68°; *α -naphthylcarbamate*, m.p. 108—109°) and γ -methylpentan- β -ol (79%) (*α -naphthylcarbamate*, m.p. 72°), respectively. (II) and MgBr_2 (1 mol.) in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ give COMeEt and other liquid products. Mixtures of *sec.*- and *tert.*-alcohol (major product, formed by rearrangement of the intermediate halogenohydrin derivative) are formed from (II) and MgMeBr and MgEtHal (Cl, Br, I). γ -Methylpentan- γ -ol (*phenylcarbamate*, m.p. 43.5°; *α -naphthylcarbamate*, m.p. 83.5°) is prepared from COMeEt and MgEtBr or MgEt_2 (small yield). The above octenone is also obtained from COMeEt and $\text{OEt}\cdot\text{MgBr}$ or MgEt_2 and from (II) and MgEtI . H. B.

Preparation of *sec.*-octyl alcohol and sebacic acid. J. M. SVETLOV and N. S. VULFSON (J. Appl. Chem. Russ., 1936, 9, 1613—1625).—*sec.*-Octyl alcohol (I) is prepared in 93—96% yield by heating castor oil (II) with NaOH [2.2 mols. per mol. of ricinoleic acid in (II)] at 112—117°. Crude (I) is best purified by successive treatment with NaHSO_3 and 5% KMnO_4 , followed by fractional distillation. Sebacic acid (III) is recovered from the residue from the initial distillation of (I) by adding half the amount of H_2SO_4 necessary to render it neutral, removing the dark, oily layer which separates, decolorising the aq. layer with active C, and neutralising the filtrate, from which impure (III), m.p. 117—122°, then separates. R. T.

Mechanism of the formation of monochlorohydrins from glycols. H. MOUREU and M. DODÉ (Compt. rend., 1936, 203, 802—804).— $(\text{CH}_2)_2\text{O}$ does not react with 0.001*N*-HCl, which indicates that it is not an intermediate in the reaction between C_2H_4 and HOCl. The rate of reaction of $\text{CHMe}\cdot\text{CH}_2$, $\text{CHEt}\cdot\text{CH}_2$, and $\text{CMe}_2\cdot\text{CH}_2$ with Cl_2 and H_2O is of the same order as for C_2H_4 , but for $\text{CHMe}\cdot\text{CHMe}$ it is much slower, probably because the latter ionises to a smaller extent than the $\alpha\beta$ -unsaturated compounds. J. L. D.

* (A., II.)

Stereoisomerism of unsaturated compounds.

II. Composition of dipropenyl glycol. W. G. YOUNG, L. LEVANAS, and Z. JASAITIS (J. Amer. Chem. Soc., 1936, 58, 2274—2276).—*trans*- $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ (A., 1932, 834) is reduced ($\text{Zn}\cdot\text{Cu}$, AcOH) to a 1:1 mixture, b.p. 113.4—114.4°/9 mm., of *meso*- and *dl*-dipropenyl glycols, since further reduction (H_2 , PtO_2 , 95% EtOH) affords a 1:1 mixture (A) of *meso*- (I), m.p. 123.5—124.5°, and *dl*- (II), b.p. 109.8—110°/9 mm., m.p. 28°, -dipropyl glycols (*bis*-3:5-dinitrobenzoates, m.p. 200.3—200.4° and 125—125.3°, respectively). The composition of (A) is determined from the m.p. curve for the *bis*-3:5-dinitrobenzoates. (I) and (II) form a eutectic, m.p. 20—20.5°, containing about 5% of (I). H. B.

Production of free radicals from ethylene oxide and the catalysis of other reactions by them.—See A., I, 35.

Explosions arising from ethers. A. F. MACCULLOCH (Chem. and Ind., 1936, 964).—A Cu wire in the container and extending to the height of the liquid effectively prevents the formation of peroxides in Et_2O . F. L. U.

Presence of free radicals in the thermal decomposition of diethyl ether.—See A., I, 36.

Cyclic acetals of butane- $\beta\gamma$ -diol. H. J. BACKER (Rec. trav. chim., 1936, 55, 1036—1039).— $(\text{CHMe}\cdot\text{OH})_2$, HCl, and the appropriate aldehyde or ketone give $\beta\gamma$ -methylene-, b.p. 102—103°, -ethylidene-, b.p. 108—109°, -isopropylidene-, b.p. 117.5—118.5°, -*sec.*-butylidene- (I), b.p. 141—143°, -benzylidene-, b.p. 117°/13 mm., -cyclohexylidene-, b.p. 79—81°/13 mm., and -4-carbethoxycyclohexylidene-dioxybutane (II), b.p. 151—152.5°/13 mm. These may be mixtures of stereoisomerides. (I) is obtained by passing $(\text{CHMe}\cdot\text{OH})_2$ over Al_2O_3 at 350—400°, by way of COMeEt which is formed by dehydration. (II) gives a mixture of isomeric derived acids, m.p. 93—101°, from which by way of the *quinine* salt an active acid (*Na* salt, $[M]_D^{20}$ -16.8°) is obtained; after recrystallisation the *Tl* salt yields an acid, m.p. 94—98°. R. S. C.

Chief constituent of the ethereal oil of *Asafœtida*. C. MANNICH and P. FRESENIUS (Arch. Pharm., 1936, 274, 461—472).—The fraction (I), b.p. 80—82°/10 mm., $[\alpha]_D^{20}$ -17.62°, of the steam-distillate of *Asafœtida* is *sec.*-Bu propenyl disulphide. The higher-boiling fraction was not obtained pure; when distilled with Zn dust, it gives a mixture, the most volatile portion of which when treated with 2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ (II) gives 4-methylthiol-*m*-dinitrobenzene. When distilled with Zn dust, (I) gives mainly *l*-*sec.*-BuSH (III), b.p. 83—84°, $[\alpha]_D^{20}$ -14.64°, and a little *sec.*-Bu propenyl sulphide (IV), b.p. 46°/20 mm. (cf. lit.). (III) is also obtained by reduction of (I) by Al-Hg, Zn-AcOH, HI-P, or Na-EtOH. Many other methods revealed the *sec.*-Bu, but not the C_3H_5 . (I) and H_2O_2 -AcOH give butane- β -sulphonic acid (*Ba* salt, dextrorotatory), which proves the disulphide nature of (I). With Na-Et₂O (I) gives a mixture of Na mercaptides, from which only (III) could be isolated and which (a) with MeI gave a partly separable mixture of Me thioethers (methiodides

inseparable), (b) with Na anthraquinone-1-sulphonate in dil. NaOH gives only 1-sec.-butylanthraquinone, m.p. 106°, but (c) with (II) in hot EtOH affords 4-1-sec.-butyl-, m.p. 65–66° [also prepared with $[\alpha]_D^{20} +1.4^\circ$ in COMe₂ from authentic (III)], and 4-propenylthiol-m-dinitrobenzene (V), m.p. 119–120°. 1-Allylanthraquinone, m.p. 143–144°, and 4-allylthiol-m-dinitrobenzene (VI), m.p. 71–72°, are prepared for comparison. (IV) in CHCl₃ with O₃ gives MeCHO and AcOH, but no CH₂O or HCO₂H, and (V) gives similarly H₂SO₄, HNO₃, MeCHO, AcOH, and a small amount of a substance, m.p. 94–95°, whereas (VI) yields CH₂O and no MeCHO; the nature of the C₃H₅ is thus proved.

R. S. C.

Reaction mechanism in the bromination of α -carboxyethyl alkyl sulphones.—See A., I, 35.

Velocity of bromination and racemisation of α -carboxyethyl alkyl sulphones.—See A., I, 35.

Photochemical reaction of chlorine with formic acid.—See A., I, 39.

Action of organic acids on their esters. H. GAULT and A. CHABLAY (Compt. rend., 1936, 203, 729–731).—The equilibration of AcOH and Me palmitate (I) is slow (9.07% MeOAc after 500 hr.), but MeOAc and palmitic acid reach equilibrium after 1000 hr. [42.7% (I) after 500 hr.]. Using in the first case 5% and in the second 0.5% H₂SO₄, equilibrium is reached in 50 and 12 hr., respectively.

R. F. P.

Reaction of benzoyl chloride with aliphatic ortho-esters and acetals. H. W. POST (J. Org. Chem., 1936, 1, 231–235).—BzCl and alkyl orthoformates give, when heated, 1 mol. each of alkyl chloride, formate, and benzoate. The yields from different esters, as determined by the yield of benzoate, are Pr^a 74, Bu^a 56, Bu ^{β} 50, *n*-C₅H₁₁ 29%. In presence of MgI₂ much HI is also formed. BzCl and CHMe(OEt)₂ give CHMeCl·OEt and EtOBz (76%); CHMe(OPr^a)₂ gives similarly a 71% yield; CH₂(OEt)₂ and BzCl give CH₂Cl·OEt and 61% of EtOBz; no HCl or olefine is formed. The following and other physical data are recorded: Bu^a₃ orthoformate, b.p. 145°/32 mm.; Pr^a, b.p. 231° (corr.)/747.6 mm., Bu^a, b.p. 129°/21 mm., Bu ^{β} , b.p. 155°/73 mm., and *n*-amyl benzoate, b.p. 167°/44 mm.

R. S. C.

Preparation of ethyl acetate from acetaldehyde in the Tischenko reaction. V. S. BATALIN, M. K. NIKITINA, S. M. RIVKIN, and E. V. SEKRETAREVA (J. Appl. Chem. Russ., 1936, 9, 1820–1831; cf. Kagan and Sobolev, A., 1933, 806).—The rate of evolution of H₂ in the reactions between Al and impure Bu^aOH in presence of HgCl₂ or Al(OBu)₃ at 92–124°, and between Al and EtOH in presence of xylene, HgCl₂, I, or Al(OEt)₃ at 140° was measured. The yield of EtOAc from MeCHO in presence of Al(OBu)₃ is higher in xylene than in EtOAc, in EtOAc higher than in Bu^aOH; it is scarcely altered by CuSO₄ or HgCl₂, but promoted by AlCl₃. In presence of Al(OEt)₃ the yield of EtOAc is 60–65% irrespective of the solvent and the additional catalysts.

J. J. B.

Solubility of thallium salts of fatty acids. Separation of solid from liquid acids. G. CAN-

NERI and D. BIGALLI (Annali Chim. Appl., 1936, 26, 430–436).—The solubilities of the Tl salts of some higher fatty acids in COMe₂, Et₂O, and EtOH have been determined at various temp. A method for the separation of solid from liquid fatty acids based on fractional crystallisation of the Tl salts from Et₂O, which may be applied to olive oil fatty acids, is described. The solubilities of the salts of the saturated acids in alcohol show wide variations.

L. A. O'N.

Addition of hydrogen chloride and iodide to olefines. Undecenoic acid. E. P. ABRAHAM and J. C. SMITH (J.C.S., 1936, 1605–1607).— κ -Chloroundecenoic acid, b.p. 148°/0.3 mm., m.p. 40.5°, and ι -chloroundecenoic acid (I), b.p. 147°/0.2 mm., m.p. 32–33°, are obtained from the κ - and ι -OH-acids, respectively, with PCl₅. Undecenoic acid (II) in C₆H₆ with FeCl₃ and HCl yields (I), also obtained with peroxide catalysts, and with NPh₃ and H₂. ι -Bromoundecenoic acid, with NaI in hot COMe₂, gives ι -iodoundecenoic acid, m.p. 22–23°, which is the sole product from (II) and HI in C₆H₆ or hexane in air, and in light petroleum with κ -epoxyundecenoic acid catalysts.

J. D. R.

Mechanism of the elaidinisation reaction. J. STUURMAN (Chem. Weekblad, 1936, 33, 700).—The experimental figures of Bertram (cf. A., 1936, 1488) are not in accord with the requirements of a termol. reaction.

S. C.

Mechanism of the elaidinisation reaction. S. H. BERTRAM (Chem. Weekblad, 1936, 33, 700–701).—Stuurman's criticism (preceding abstract) is unjustified.

S. C.

Experiments towards synthesis of isofenchone and its degradation products. S. K. RANGANATHAN (Current Sci., 1936, 5, 198).—Et α -dimethyl-lævulate, b.p. 108–110°/25 mm. (semicarbazone, m.p. 154°; 2:4-dinitrophenylhydrazone, m.p. 98°), with Zn and CH₂Br·CO₂Et gives Et β -hydroxy- β - δ -trimethyladipate lactone, b.p. 137–138°/6 mm., which with KCN at 220° affords an ester, hydrolysed by conc. HCl to $\beta\beta$ -dimethylpentane- $\beta\delta\epsilon$ -tricarboxylic acid, m.p. 172°, the Et₃ ester, b.p. 125–128°/1–2 mm., of which is cyclised.

R. S. C.

Micro-determination of glycuronic acid. O. FÜRTH and K. PESCHEK (Biochem. Z., 1936, 287, 365–379).—The substance containing glycuronic acid (I) is heated in a distillation apparatus at 175–190° with Sn and 85% H₃PO₄ in a stream of H₂ and the furfuraldehyde (II) in the distillate determined colorimetrically. Numerous experiments with (I) lactone, euxanthic acid, borneol- and menthol-(I), and the semicarbazone and K salt of (I) yield 40–46% (mean 43.8%) of the theoretical amounts of (II) and the figure obtained must be multiplied by 2.3 to convert into (II) and by 4.6 to convert into (I). The yields of (II) are > by the usual HCl distillation method (31%). Xylose gives 100% and arabinose 66% of the expected amount of (II). Glucose and glucosamine both give considerable amounts of (II) and the method cannot be used in presence of carbohydrate. With substances of wholly unknown (I) content, it is better to determine the (II) produced

by iodometric titration. In a third method, (I) is calc. from the amount of CO_2 evolved when (I) is decomposed with mineral acid. This method is more sp., but on the micro-scale the individual differences in parallel determinations are greater (85—105% of theory). P. W. C.

Methylthiolacetic acid and mercuric chloride. N. HELLSTRÖM and B. HOLMBERG (Arkiv Kemi, Min., Geol., 1936, 12, A, No. 2, 9 pp.).—Interaction of $0.1N\text{-SMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ with cold $0.4N\text{-HgCl}_2$ affords the substance, $\text{SMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{HgCl}\cdot\text{HgCl}_2$, which darkens at 150° , not melting at 200° . At 100° , determination of the wt. of the ppt. (composition $\text{SMe}\cdot\text{HgCl} + 2\text{HgCl}$) and acidity formed after different periods of heating shows the occurrence of the reaction $\text{SMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) + $3\text{HgCl}_2 + \text{H}_2\text{O} = \text{SMe}\cdot\text{HgCl} + 2\text{HgCl} + \text{CHO}\cdot\text{CO}_2\text{H}$ (II) + 3HCl . The reaction velocity is decreased by H^+ and especially by Cl^- addition, the reacting entities being the acid anion and Hg^{++} . The first stage is (I) + $2\text{HgCl}_2 + \text{H}_2\text{O} = \text{SOMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III) + $2\text{HgCl} + 2\text{HCl}$, but (III) is too unstable to be isolated. Oxidation of (I) with $\text{K}_2\text{S}_2\text{O}_8$, acidification, and evaporation at room temp. gives *dimethylthiolacetic acid*, m.p. $79\text{--}81^\circ$. Warming in acid solution causes fission to MeSH and (II), and in the presence of HgCl_2 a ppt. of $\text{SMe}\cdot\text{HgCl}$ (or its mixture with HgCl) results from its interaction with MeSH , thus preventing by-product formation. J. W. B.

Production of *d*- and *l*- α -hydroxy- γ -methylthiolbutyric acids.—See A., III, 34.

Method of extracting aldehydes and ketones from their hydrogen sulphite compounds. A. BARBOT (Compt. rend., 1936, 203, 728—729).—By adding a slight excess of CH_2O to aq. solutions or suspensions of aldehyde or ketone H sulphites at 100° complete cleavage is obtained without the side reactions which occur in acidic or alkaline methods. R. F. P.

Catalysis of formaldehyde to reducing sugars by ascorbic acid. E. S. WEST and L. F. NEY (Science, 1936, 84, 294).—Ascorbic acid (I) actively catalyses the production of reducing sugars from CH_2O in presence of $\text{Ca}(\text{OH})_2$, supporting the view that (I) contains the one-diol group. (I) combines with CH_2O even in acid solution and may be an active photosynthetic catalyst. L. S. T.

Thermal decomposition of acetaldehyde and ethylene oxide.—See A., I, 34.

Polymorphism of acetaldehyde-2:4-dinitrophenylhydrazone. W. M. D. BRYANT (J. Amer. Chem. Soc., 1936, 58, 2335; cf. A., 1932, 1109; 1933, 1005).—In agreement with Ingold *et al.* (A., 1934, 278) and contrary to Campbell (A., 1936, 1005), acetaldehyde-2:4-dinitrophenylhydrazone exists in two forms, m.p. 147° and 168.5° , which are optically indistinguishable. H. B.

Synthesis of an asymmetric aliphatic allene molecule by means of an acetylene-allene isomerisation. A. E. FAVORSKI and P. A. FICHOMOLOV (Compt. rend., 1936, 203, 726—727; cf. A., 1935, 605).—In disubstituted acetylenes containing a *tert.* substituent a migration of the β -H occurs giving rise

to allenes; when the substituent possesses a functional grouping the mol. obtained is capable of optical resolution. $\text{CBu}^t\text{:C}\cdot\text{MgBr}$ and $\text{COMe}\cdot\text{CH}_2\text{Cl}$ give α -chloro- β - ϵ -trimethyl- Δ^7 -hexen- β -ol, m.p. $29\text{--}31^\circ$, b.p. $66^\circ/15\text{ mm.}$, which with powdered K in Et_2O affords α - β -oxido- β - ϵ -trimethyl- Δ^7 -hexinene (I), b.p. $154\text{--}156^\circ$. (I) with ZnCl_2 yields α δ δ -trimethyl- Δ^8 -hexinene, which rearranges to α δ δ -trimethyl- Δ^8 -hexadienal, b.p. $58\text{--}59^\circ/20\text{ mm.}$ (semicarbazone, m.p. $156\text{--}157^\circ$).

R. F. P.

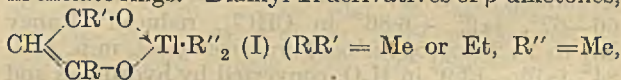
Rapid approximate determination of ketones. E. K. NIKITIN (J. Appl. Chem. Russ., 1936, 9, 1704—1710).—The method previously described for determination of furfuraldehyde (A., 1936, 1006) is applied to determination of ketones (COMeEt , COMePr , COPhMe). R. T.

Determination of acetone by means of its reaction with furfuraldehyde. E. K. NIKITIN and I. I. PAUL (J. Appl. Chem. Russ., 1936, 9, 1711—1715).—A mixture of 10 ml. each of aq. COMe_2 , 0.2% furfuraldehyde, and 10% KOH is shaken, and maintained at room temp. for 10—15 min. 20 ml. of 60% H_2SO_4 are added to 10 ml. of the mixture, and the intensity of coloration is compared with that given by standard aq. COMe_2 . The error is 0 for concns. $\leq 0.005\%$ and $+3\%$ for 0.001% COMe_2 . R. T.

Capacity for reduction of the keto-group on graphite.—See A., I, 38.

Photo-reactions of liquid and dissolved ketones. III.—See A., I, 39.

Application of thallium compounds in organic chemistry. X. Influence of change of substituent on the properties of chelate rings. R. C. MENZIES and A. R. P. WALKER (J.C.S., 1936, 1678—1685).—Previous conclusions (A., 1932, 1269; 1933, 56, 267) are discussed from the point of view of changes in properties caused by changes of substituents in chelate rings. Dialkyl Tl derivatives of β -diketones,



Heavy oxygen content of carbohydrates.—See A., I, 41.

Colour reactions of carbohydrates. I. Spectrophotometric examination of the common colour reactions. T. NOZOE (J. Chem. Soc. Japan, 1935, 56, 852—863).—Absorption data are given. The effects of [HCl], catalysts, and of heat were studied. CH. ABS. (c)

Determination of reducing sugars by the alkalimetric method of Rosenthaler and Curli. Y. VOLMAR and S. KLEIN (J. Pharm. Chim., 1936, [viii], 24, 400—409).—In Curli's method (B., 1935, 519) for the determination of reducing sugars, if the amount of sugar is > 0.15 g. the decrease in alkalinity (n c.c. of N -NaOH) is related to the wt. of glucose (m) in the 25-c.c. sample by $m = Kn$. For all the hexoses examined and for arabinose $K = 1.23$. For larger amounts of sugar the vals. so obtained are too large. The method may be used for invert sugar from sucrose ($K = 1.23$), and for lactose ($K = 1.8$) and maltose ($K = 2.2$). J. W. B.

Preparation of furanose derivatives of pentoses. *iso*Propylidene-*l*-arabofuranoside. P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1936, 116, 189—202).—*l*-Arabinose Et_2 mercaptal with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}\cdot\text{C}_5\text{H}_5\text{N}$ at 0° gives its 5-*p*-toluenesulphonate (I), m.p. 65—66°, $[\alpha]_D^{25} + 49.05^\circ$ in CHCl_3 , hydrolysed (aq. $\text{COMe}_2\text{-CdCO}_3\text{-HgCl}_2$) to *l*-arabofuranose 5-*p*-toluenesulphonate (II) [*phenylhydrazone*, m.p. 115—116° (decomp.), $[\alpha]_D^{25} + 6.31^\circ$ to 18.9° in $\text{C}_5\text{H}_5\text{N}$], the 1:2-*isopropylidene* derivative (III), m.p. 129—130°, $[\alpha]_D^{25} - 34.8^\circ$ in CHCl_3 , of which is converted by Na-Hg-80\% MeOH into 1:2-*isopropylidene-l*-arabofuranose (IV), m.p. 117—118°, $[\alpha]_D^{25} - 28.9^\circ$ in H_2O . (II) is converted by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ at 0° into its Ac_2 derivative, converted by $\text{NaI}\cdot\text{COMe}_2$ at 100° into 5-*iodo*-, converted by $\text{AgNO}_3\text{-MeCN}$ at 100° into 5-*nitro-l*-arabinose triacetate, b.p. 145—150°/0.05 mm. (III) is similarly converted into the 5-*I*-compound, m.p. 66—67°, $[\alpha]_D^{27} + 6.86^\circ$ in CHCl_3 , reduced (Raney Ni) to 1:2-*isopropylidene-l*-arabomethyllose, m.p. 83—84°, $[\alpha]_D^{25} - 13.9^\circ$ in H_2O , converted by hydrolysis and EtSH into *l*-arabomethyllose Et_2 mercaptal, m.p. 108—109°, $[\alpha]_D^{20} + 11.9^\circ$ in $\text{C}_5\text{H}_5\text{N}$. (I) with hot $\text{HgCl}_2\text{-MeOH}$ gives *Me l*-arabinoside 5-*p*-toluenesulphonate, the 2:3- Ac_2 derivative of which is converted into the 5-*I*-compound, reductive hydrolysis (Raney Ni-NaOH) of which gives α -methyl-*l*-arabomethylloside, b.p. 95—100°/0.3 mm., m.p. 88—89°, $[\alpha]_D^{25} - 130.0^\circ$ in CHCl_3 . Comparison of the rates of hydrolysis of (IV) and 1:2:3:4-diisopropylidene-*l*-arabinose confirms the pyranose structure of the latter. J. W. B.

Reduction of acetobromoarabinose by zinc and acetic acid. G. E. FELTON (J. Amer. Chem. Soc., 1936, 58, 2313—2314).—Reduction (method: Levene and Mori, A., 1929, 1277) of acetobromoarabinose gives arabinol diacetate, arabinose triacetate, and a little of the *tetra*-acetate (I), interconvertible forms, m.p. 167—169° (from C_6H_6) and 184.5—185.5° (from EtOH), $[\alpha]_D^{25} + 69.5^\circ$ in CHCl_3 , of a *disaccharide* (II), $\text{C}_{10}\text{H}_{18}\text{O}_7$, m.p. 177—180° (decomp.), derived from a deoxypentose. (I) and (II) do not reduce Fehling's

solution; acid hydrolysis gives reducing substances in both cases. H. B.

Action of hydrogen peroxide on *l*-xyloketose (urine pentose). M. ENKLEWITZ (J. Biol. Chem., 1936, 116, 47—49).—Addition of 3% H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, or $\text{K}_2\text{Cr}_2\text{O}_7$ to pentose urine at room temp. causes a rapid loss of reducing properties. Pure xyloketose in aq. solution is not so reactive, and solutions of other sugars in urine and in H_2O are not affected by cold 3% H_2O_2 . J. N. A.

Synthesis of *d*-allomethyllose by a series of Walden inversions accompanying alkaline hydrolysis of *isopropylidene-l*-rhamnose 5-*p*-toluenesulphonate. P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1936, 116, 169—188).—2:3-*iso*Propylidene- β -*l*-rhamnose with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}\cdot\text{C}_5\text{H}_5\text{N}$ in CHCl_3 at 0° gives its 5-*p*-toluenesulphonate (I), m.p. 92—93°, $[\alpha]_D^{24} + 29.1^\circ$ in CHCl_3 , converted by MeOH-HCl into 5-*p*-toluenesulphonyl-2:3-*isopropylidene-methyl-l*-rhamnofuranoside, m.p. 83—84°, $[\alpha]_D^{25} - 14.28^\circ$ in MeOH . Hydrolysis of (I) with NaOMe-MeOH at room temp. occurs with Walden inversion to give 2:3-*isopropylidenemethyl-d*-allomethylfuranoside (II), b.p. 85—86°/0.3 mm., m.p. 22°, $[\alpha]_D^{23} - 78.1^\circ$ in MeOH , purified through its 5-*p*-toluenesulphonate, m.p. 93—94°, $[\alpha]_D^{24} - 46.8^\circ$ in MeOH , and hydrolysed by 1.5% H_2SO_4 at 100° to *d*-allomethyllose (III), m.p. 151—152°, $[\alpha]_D^{24} - 8.5^\circ$ to $+1.2^\circ$ in H_2O (Micheel, A., 1930, 455) (*p*-bromophenylhydrazone, m.p. 145—146°, $[\alpha]_D^{27} - 21.9^\circ$ to -11.8° in $\text{C}_5\text{H}_5\text{N}$; phenyllosazone, m.p. 184—185°, $[\alpha]_D^{25} - 79.1^\circ$ to -49.4° in $\text{C}_5\text{H}_5\text{N-EtOH}$). The constitution of (III) follows from its conversion (MeOH-HCl) into α -, b.p. 105—106°/0.3 mm., $[\alpha]_D^{23} + 54.2^\circ$ in H_2O , and β -methyl-*d*-allomethylpyranoside, m.p. 94—95°, $[\alpha]_D^{25} - 61.26^\circ$ in H_2O , further methylated ($\text{Me}_2\text{SO}_4\text{-60\% NaOH}$ at 55—75°) to its 2:3:4-*Me*₃ derivative, b.p. 60—62°/0.3 mm., $[\alpha]_D^{22} - 43.5^\circ$ in H_2O , oxidised by HNO_3 (*d* 1.42) to *i*-trimethoxyriboglutaric acid, isolated as its *Me*₂ ester, b.p. 110—112°/0.3 mm., and characterised as its *di*-methylamide, m.p. 145—146°, identical with a specimen prepared from 2:3:4-trimethylribose, new m.p. 98—100°. The ring structure in (II) is confirmed by comparison of its rate of hydrolysis with 0.03*N*-HCl at 100° with that of the corresponding *l*-rhamnofuranoside and by methylation ($\text{Ag}_2\text{O-MeI}$) of (II) to its 5-*Me* derivative, b.p. 85—86°/0.3 mm., $[\alpha]_D^{23} - 78.4^\circ$ in MeOH , hydrolysed by 1% H_2SO_4 at 100° to 5-methyl-*d*-allomethyllose, converted into 2:3:5-trimethylmethyl-*d*-allomethylloside, b.p. 78—80°/0.3 mm., oxidised by HNO_3 (*d* 1.42) to *i*-dimethoxysuccinic acid. J. W. B.

Preparation and properties of xyloseen-(1:2) tribenzoate. R. T. MAJOR and E. W. COOK (J. Amer. Chem. Soc., 1936, 58, 2333—2334).— α -*d*-Xylose tetrabenzoate, m.p. 115—116°, $[\alpha]_D^{20} + 115^\circ$ (all rotations are in CHCl_3) (from *d*-xylose and BzCl in cold $\text{CHCl}_3\text{-C}_5\text{H}_5\text{N}$), with AcOH-HBr in CHCl_3 -dioxan gives *bromobenzo-d*-xylose, m.p. 134—135°, $[\alpha]_D^{20} + 117^\circ$, converted by Ag_2CO_3 in COMe_2 a little H_2O into *d*-xylose tribenzoate, m.p. 188—189°, $[\alpha]_D^{20} + 39.5^\circ$, and by NH_4Et_2 in C_6H_6 at 55° into *d*-xyloseen-(1:2) tribenzoate, m.p. 126—128°, $[\alpha]_D^{20} - 280^\circ$. α -*l*-Xylose tetrabenzoate, m.p. 115—116°, $[\alpha]_D^{20} - 115^\circ$ (β -form, m.p. 173—174°, $[\alpha]_D^{20} + 44.5^\circ$, obtained once

when the reaction product was crystallised from EtOH- C_5H_5N , similarly affords *bromobenzo-l-xylose*, m.p. 134—135°, $[\alpha]_D^{20}$ -116°, and thence *l-xyloseen*-(1:2) tribenzoate, m.p. 126—128°, $[\alpha]_D^{20}$ +280° (*dichloride*, m.p. 178—180°, $[\alpha]_D^{20}$ +110°). H. B.

Preparation of osones. L. BRÜLL (Annali Chim. Appl., 1936, 26, 415—417).— $AcCO_2H$ is substituted for $PhCHO$ in the removal of the hydrazinic residue from osazones. $AcCO_2H$ liberates $PhCHO$ itself from $CHPh:N:NHPh$. Yields are increased to 75% for glucose and 40% for xylose. L. A. O'N.

Influence of concentration of glucose solution, and of the proportion of iodine necessary for oxidation to that actually used, on the results given by Willstätter and Schudel's method. S. S. ALESCHIN (J. Appl. Chem. Russ., 1936, 9, 1729—1730).—Trustworthy results are obtained with solutions containing < 50 mg. of glucose, in concn. < 0.05%. Excess of I does not interfere, a 50% excess being desirable. The velocity of reaction is independent of the glucose concn. R. T.

Polymorphism of sucrose octa-acetate. M. FRÈREJACQUE (Compt. rend., 1936, 203, 731—733).—Addition of H_2O to sucrose octa-acetate form I (Pictet, A., 1936, 1166) in EtOH yields form III, m.p. 87°, also obtained from solutions of form I in CS_2 . Both these forms have the same rotation and rotatory dispersion in $CHCl_3$, but the crystallographic indices are different. R. F. P.

Verbenalin. J. CHEYMOL (Compt. rend., 1936, 203, 814—816).—Verbenalin (*oxime*, decomp. 155°; *phenylhydrazone*) has a strongly reducing CO and contains 1 OMe; with emulsin it affords glucose and verbenalinol (cf. A., 1936, 1366). It is a lactone easily hydrolysed by $Ba(OH)_2$ to *verbenallosidic acid*, $C_{11}H_{26}O_{11}$ (Ba and Na salts), which is strongly reducing and is further hydrolysed by dil. acid or emulsin. J. L. D.

Glucosides of the flavone series. III. **Constituents of *Trifolium repens*.** L. T. NAKAOKI (J. Pharm. Soc. Japan, 1933, 53, 1114—1121).—From the flowers *trifolin* (I), $C_{21}H_{22}O_{12} \cdot 3H_2O$, m.p. 228—229°, an isomeride, *isotrifolin*, an *isorhamnetin glucoside*, and a *substance*, m.p. 240°, are isolated. (I) on hydrolysis yields quercetin and rhamnose and is thus quercetin rhamnoside. CH. ABS. (r)

Constituents of *Epimedium macranthum*. Morr and Decne. II. **Constitution of a new flavone glucoside.** 2. **Relationship between icaritin, anhydroicaritin, and β -anhydroicaritin and oxidation of anhydroicaritin.** S. AKAI and T. MATSUKAWA. III. 3. **Synthesis of anhydroicaritol and anhydroicaritin trimethyl ether.** S. AKAI and K. NAKAZAWA (J. Pharm. Soc. Japan, 1935, 55, 705—719, 719—727).—II. Corrections are made to earlier work (A., 1936, 710). Anhydroicaritin Me_3 ether hydrochloride yields anhydroicaritin Me_3 ether (I) with $C_5H_5N-Na_2CO_3$ and icaritin Me_3 ether (II) with NaOH. Anhydroicaritin (III) with dry HCl affords β -anhydroicaritin. With $KMnO_4$ and with O_3 , (I) and (II) yield $COMe_2$ and anisic acid. Ozonolysis of anhydroicaritol affords *icaritolic acid*, $C_{10}H_7O_4(OMe)_3$, m.p. 212°. (III) with H_2O_2 yields

anisic acid, whereas (I) with H_2O_2 yields a *substance*, $C_{24}H_{26}O_6(OH)_2$, m.p. 231°. With EtOH-KOH (II) yields icaritol (*oxime*, m.p. about 160°).

III. Myricetin Me_3 ether with EtOH-KOH followed by CO_2 yields 2-hydroxy-4:6- ω -trimethoxyacetophenone, m.p. 102°; this with Na and $\gamma\gamma$ -dimethylallyl bromide in C_6H_6 yields 2-hydroxy-4:6:6'- ω -trimethoxy-3-($\gamma\gamma$ -dimethylallyl)acetophenone (I), m.p. 128°, identical with anhydroicaritol, the corresponding 2-($\gamma\gamma$ -dimethylallyl) compound, m.p. 62—63°, being obtained as a by-product. (I) with Na anisate and anisic acid yields anhydroicaritin Me_3 ether, m.p. 154°.

CH. ABS. (r)

Anthraquinone colouring matters: ruberythric acid. D. RICHTER (J.C.S., 1936, 1701—1703).—Enzymic hydrolysis of ruberythric acid (I) gives primeverose, chemical identification of which was confirmed by crystallographic comparison with a pure specimen. (I) gives alizarin 1-Me ether on methylation ($Ag_2O-MeI-COMe_2$), followed by hydrolysis ($AcOH-HCl-H_2O$), and is readily hydrolysed by hetero- β -glucosidases. It is therefore 2- O - β -primeverosido-alizarin (cf. A., 1933, 1146). H. G. M.

Molecular structure of glycogen from whole tissues of *Mytilus edulis*.—See A., III, 7.

Association of xylan with cellulose in certain structural celluloses.—See A., III, 52.

Highly-polymerised compounds. CXLVII. **Degree of polymerisation of natural and technical celluloses.** H. STAUDINGER and K. FEUERSTEIN (Annalen, 1936, 526, 72—102).—The fibres are extracted successively with H_2O , EtOH, C_6H_6 , and $COMe_2$, dried in a high vac., and the viscosity of their dil. solutions in Schweitzer's reagent is measured. After dissolution in the same reagent and reprecipitation in the dark and absence of air, the measurements are repeated, whereby little alteration is observed. The degree of polymerisation of cotton, ramie, flax, hemp, manila, sisal, nettle, and jute is about 2000; a similar val. is obtained for synthetic β -cellulose from sucrose and *B. xylinum*. The cellulose from young plants, after purification as outlined above (which does not remove all the impurities), has 1000 as degree of polymerisation, except in the case of rye-straw cellulose, which has about 1600. Wood, according to its kind, yields only 1—6% of cellulose to Schweitzer's reagent with degree of polymerisation > 1600. Wood cellulose appears therefore highly complex and similar to fibre cellulose. Treatment of wood with $Ca(HSO_3)_2$ involves a glucosidic degradation of the long cellulose mols., and subsequent bleaching involves oxidative decomp. Short treatment leaves a slightly degraded material contaminated with other wood components. Longer treatment gives a purer but more degraded product. The most complex portions (α -cellulose) retain the physical characteristics of cellulose, are insol. in NaOH, and have a degree of polymerisation > 200; β - and γ -cellulose are sol. in NaOH, the degree of polymerisation of the latter being < 10. Viscose and Cellophane from pine cellulose, degree of polymerisation 700—900, have degree of polymerisation 300—400 and about 300, respectively. Linters, 1400, depressed by bleaching to 700, gives a Cu or

acetate silk, 400—500. The cellulose of nitro-silk is greatly degraded. The relationship between the physical properties and the degree of polymerisation of cellulose is discussed. H. W.

Condensation of cellulose with benzene. A. A. NIKOLSKI (J. Gen. Chem. Russ., 1936, 6, 1151—1156).—The fractions of b.p. 120—350°, obtained by dry distillation of the product of condensation of cellulose in conc. H_2SO_4 and C_6H_6 , contain CH_2Ph_2 , PhMe , C_{10}H_8 , anthracene 2:2-diphenyl-2:3-dihydrofuran, diphenyl-1:4-pyran, and 6-methyl-1:4-benzopyran. R. T.

Ammonium salts from bromopropylamines. VI. Salts of polymeric tertiary amines. J. C. COWAN and C. S. MARVEL (J. Amer. Chem. Soc., 1936, 58, 2277—2279; cf. A., 1935, 965).— γ -Phenoxypropyl bromide and an excess of the appropriate NH_2Alk give *N*-methyl-, b.p. 133—138°/23 mm. (hydrochloride, m.p. 155—156°; hydrobromide, m.p. 150—151°), -ethyl-, b.p. 147—148°/26 mm. (hydrobromide, m.p. 154—155°), -*n*-propyl-, b.p. 154—155°/25 mm. (hydrobromide, m.p. 160—161°), -*n*-butyl-, b.p. 134—135°/5 mm. (hydrobromide, m.p. 170—171°), and -isobutyl-, b.p. 153—156°/20 mm. (hydrobromide, m.p. 174—175°), - γ -phenoxypropylamine, which are converted by 48% HBr at 137—142° (bath) into *N*-methyl-, b.p. 29—30°/4 mm. (hydrobromide, m.p. 64—66°), -ethyl-, b.p. 31—32°/2 mm. (hydrobromide, m.p. 144—146°), -*n*-propyl-, b.p. 37—38°/3 mm. (hydrobromide, m.p. 225—226°), -*n*-butyl- [hydrobromide, m.p. 253—255° (Maquenne)], and -isobutyl- [hydrobromide, m.p. 255—257° (Maquenne)], - γ -bromopropylamine, respectively. Conc. solutions of these Br-amines in (usually) 95% EtOH polymerise fairly rapidly to salts of the type $\{\text{Br}[(\text{CH}_2)_3\text{NHR}]^+_n(\text{CH}_2)_3\text{NHR}\}_n\text{Br}^-$ (I) [$\text{R} = \text{Me}$, m.p. 205—210° (decomp.); Et , m.p. 195—199°; Bu^a , m.p. 100—120°]; mol. wts. vary from 1350—1550 ($\text{R} = \text{Bu}^a$) to 10,800—15,200 ($\text{R} = \text{Me}$). (I) ($\text{R} = \text{Me}$) with $\text{Ag}_2\text{O}-\text{H}_2\text{O}$ gives the hygroscopic base, which has p_H about 9.3 in 0.1*N* solution. Polymerisation of the amines in dil. solution results in the formation of complex products. H. B.

Polyiodides of hexamethyl- α,γ -diaminoisopropyl alcohol di-iodide. M. COVELLO (Annali Chim. Appl., 1936, 26, 405—408).—The polyiodides R_nI_4 , m.p. 149.5°, R_nI_6 , m.p. 152°, and R_nI_8 , decomp. 136°, have been prepared by the action of KI_3 on the di-iodide, $\text{R} = \text{OH}\cdot\text{CH}(\text{CH}_2\text{NMe}_3\text{I})_2$ (cf. B., 1925, 378), and their equilibria in solution studied.

L. A. O'N.

Amino-sugar of heparin. E. JORPES and S. BERGSTRÖM (Z. physiol. Chem., 1936, 244, 253—256).—Glucosamine in 50% yield is obtained from purified protein-free heparin (I) by heating for 6 hr. at 100° with conc. HCl . Chondroitinsulphuric acid treated in the same way with 20% HCl at 135° for 8 hr. gives chondrosamine in 61% yield. The uronic acid of (I) is probably glycuronic acid. Hence (I) is probably a mucoitinpolysulphuric acid. W. McC.

Reaction of formaldehyde with amino-acids. A. WADSWORTH and M. C. PANGBORN (J. Biol. Chem., 1936, 116, 423—436).—The reaction between 8 NH_2 -acids, guanidine (I), alanyl-glycine (II), glycylalanine (III), peptone, and a crude diphtheria toxin in 0.5*M*-

solution and CH_2O equiv. to the $\text{NH}_2\text{-N}$ present at p_H 7.8—8.4 and 39° has been investigated by periodic determination of $\text{NH}_2\text{-N}$ (Van Slyke), free CH_2O (as its dimedon compound), and reversibly bound CH_2O (3 days' contact with dimedon at p_H 4.8 and 39°). The greatest affinity for CH_2O is shown by histidine, tryptophan (IV), arginine (V), and cysteine, whilst the second CO_2H in aspartic and glutamic acids greatly decreases reactivity. Alanine and glycine are much less reactive than (II) and (III). Continued incubation usually decreases the % of total combined CH_2O which can be split off by dimedon, (I) and (V) being exceptions, and no reversal of the reaction could be detected with (II) and (III). In alkaline solution dimedon causes no reversal and fails to prevent continued condensation between CH_2O and NH_2 . The reaction product with (IV) was isolated and identified as 3:4:5:6-tetrahydro-4-carboline-5-carboxylic acid (Jacobs *et al.*, A., 1936, 742). Mechanism is discussed, and it is concluded that the reaction comprises a rapid reversible reaction followed by a slower irreversible one in which rearrangement to a stable compound with CH_2O occurs. J. W. B.

High-vacuum distillation of *N*-acyl-amino-acid and -polypeptide esters. S. GURIN (J. Amer. Chem. Soc., 1936, 58, 2104—2106).—*N*-Benzenesulphonyl and *N*- CO_2Et -derivatives of esters (*Et*, *Bu*) of NH_2 -acids and di- and tri-peptides can be distilled (usually without decomp.) at pressures of 10^{-6} to 10^{-7} mm.; racemisation does not occur. The following are prepared [usually by the method previously described (A., 1935, 101)]: benzenesulphonyl-glycyl-dl-alanine (I), m.p. 74°, -dl-leucylglycylglycine (II), m.p. 171°, and -dl-methionine (III), m.p. 45°, *Et* esters; dibenzenesulphonylcystine *Et_2* ester (IV), m.p. 121° (not distillable); carbethoxyglycylglycine *Et* ester (V), m.p. 86°; benzenesulphonyl-dl-alanyllalanine, m.p. 102°, -dl-phenylalanine, m.p. 107°, and -dl-serine, m.p. 55°, *Bu* esters; dibenzenesulphonyl-1-tyrosine *Bu* ester, m.p. 98°, $[\alpha]_D^{25} +20.2^\circ$ in EtOH . All m.p. are corr. The following mixtures are separable (90% recovery) by fractionation: (I) + (II); (III) + (IV); (V) + carbethoxydiglycylglycine *Et* ester; benzenesulphonyl-glycine + -dl-alanine *Bu* esters. H. B.

Compounds of amino-acids with organic (especially fatty) acids. I. S. J. VON PRZYBYCKI and K. KASPRZYK. II. Amino-acids or peptides and the higher fatty acids. E. HOFER (Biochem. Z., 1936, 288, 29—38, 39—40).—I. Pptn. reactions (Et_2O , C_6H_6), Tyndall effect, and crystallising properties of solutions of NH_2 -acids (I) in presence of AcOH , PrCO_2H , $\text{H}_2\text{C}_2\text{O}_4$, and hexoic and oleic acid (II) indicate the formation in H_2O -free systems of compounds of basic (I) only, whilst in aq. solution both basic and neutral (I) combine with fatty acids in mol. proportions of 1:2 or 3 and 1:1, respectively. In solid systems, fatty acids form salts only with basic (I) (cf. Jukes and Schmidt, A., 1935, 966).

II. (I) and leucylglycylglycine do not influence σ of (II)- H_2O . Basic (I) (e.g., arginine and guanidine) and diglycylglycine, but not neutral or acidic (I), enhance emulsion formation of (II)- H_2O at p_H 3—4. The probable formation of compounds of (II) with basic (I) and peptides is discussed. F. O. H.

Helianthates of amino-acid and polypeptide esters. S. GURIN and C. F. SEGAL (J. Amer. Chem. Soc., 1936, 58, 2107—2109).— NH_2 -acid and polypeptide ester hydrochlorides with methyl-orange in H_2O give good yields of cryst., non-hygroscopic ester helianthates, also prepared from the free esters and helianthin (I). The free acids do not afford similar salts. The following are described: *glycine* (II), m.p. 203° (decomp.), *alanine*, m.p. 211.5° (decomp.), *l-leucine*, m.p. 210.5° (decomp.), *phenylalanine*, m.p. 210° (decomp.), *l-tyrosine*, m.p. 209° (decomp.), *methionine*, m.p. 210.5° (decomp.), *glycylglycine*, m.p. 210° (decomp.), *glycyl-l-leucine*, m.p. 216° (decomp.), *diglycylglycine*, m.p. 215° (decomp.), and *leucylglycylglycine*, m.p. 187° (decomp.), *Et* ester helianthates; *alanine*, m.p. 201.5° (decomp.), *alanyl-alanine*, m.p. 210° (decomp.), *glycylalanine*, and *alanylglycine*, m.p. 210° (decomp.), *Bu* ester helianthates; *Bu*, *d*-glutamate helianthate, m.p. 199° (decomp.); *d*-lysine *Me*, m.p. 242.5° , α -glycyl-*d*-lysine *Me*, m.p. 232.5° , *l*-histidine *Me*, m.p. 221° , *d*-arginine *Me*, m.p. 229.5° , and *l*-cystine *Et*, m.p. 212° , ester dihelianthates; ϵ -carbobenzyloxy-*d*-lysine *Me* ester helianthate, m.p. 183° ; *guanidine helianthate*, m.p. 270° . The amount of (I) in these salts is determined colorimetrically in 50% aq. AcOH. $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$ is recovered in 79% yield from (II) and dry HCl in EtOH. *Bu* esters of NH_2 -acids and polypeptides are prepared by vac. distillation with an excess of BuOH at $<55^\circ$ in presence of sufficient mineral acid for neutralisation of the NH_2 -groups. Hygroscopic, H_2O -sol. salts are obtained from the esters and EtSO_3H , $\text{Bu}^+\text{SO}_3\text{H}$, $\text{CH}_2\text{Ph}\cdot\text{SO}_3\text{H}$, *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, and *d*-camphor-10-sulphonic acid. H. B.

Colour reaction of glycine with ferric chloride. I. J. V. DUBSKÝ and A. LANGER (Coll. Czech. Chem. Comm., 1936, 8, 435—445).—When FeCl_3 (1 mol.) and glycine (I) (0.5 mol.) in a little H_2O are evaporated at 50° and the residue is extracted with EtOH, the compound, $\text{OH}\cdot\text{FeCl}_2\cdot\text{FeCl}_3\cdot 2(\text{I})\cdot 3\text{H}_2\text{O}$, m.p. 127° (decomp.), is obtained. 1 mol. each of FeCl_3 and (I) in a little H_2O deposit a mixture, converted by EtOH into the compound, $\text{OH}\cdot\text{FeCl}_2\cdot 2\text{FeCl}_3\cdot 4(\text{I})\cdot 5\text{H}_2\text{O}$, m.p. 174° (decomp. from 176°), which with EtOH gives an insol. compound, $2\text{OH}\cdot\text{FeCl}_2\cdot\text{FeCl}_3\cdot 4(\text{I})\cdot 6\text{H}_2\text{O}$, m.p. 115° (decomp.), and from the filtrate a cryst. mixture separates, which is converted by 96% EtOH into the compound, $\text{OH}\cdot\text{FeCl}_2\cdot\text{FeCl}_3\cdot (\text{I})\cdot 3\text{H}_2\text{O}$, softens at 110° , decomp. 125° . When, however, FeCl_3 and (I) (1 mol.) in H_2O are evaporated and the residue is extracted with EtOH, there is obtained a compound, $2\text{OH}\cdot\text{FeCl}_2\cdot\text{FeCl}_3\cdot 4(\text{I})\cdot \text{H}_2\text{O}$, decomp. 120° . FeCl_3 and (I) (1.5 mol.) in H_2O deposit an impure compound, $\text{OH}\cdot\text{FeCl}_2\cdot\text{FeCl}_3\cdot 3(\text{I})\cdot 3\text{H}_2\text{O}$, m.p. 112° (decomp.), converted by EtOH into the hydrate, $+2.5\text{H}_2\text{O}$, m.p. 175° (decomp.), which in H_2O gives the dihydrate, m.p. 173° (decomp.). When FeCl_3 and (I) (1.66 mol.) are evaporated in H_2O and the residue is extracted with EtOH, the compound, $\text{OH}\cdot\text{FeCl}_2\cdot\text{FeCl}_3\cdot 3(\text{I})\cdot 4\text{H}_2\text{O}$, decomp. 178° , is obtained; 2 mols. of (I) give similarly the compound, $\text{OH}\cdot\text{FeCl}_2\cdot\text{FeCl}_3\cdot 4(\text{I})\cdot 4\text{H}_2\text{O}$, decomp. 123° . If 3 mols. of (I) are used, only (I) or its hydrochloride crystallises. The solid compounds are yellow to black, but give red solutions. R. S. C.

Interaction of iodoacetic acid and tertiary amines. M. P. SCHUBERT (J. Biol. Chem., 1936, 116, 437—445).—Kinetic investigation (by Volhard determination of I) of the interaction of $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ (I) and $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{NH}_2$ (II) with the various possible derivatives of the type NR_3 ($\text{R} = \text{H}$, *Me*, or $\text{CH}_2\cdot\text{CO}_2\text{H}$) and with certain cyclic bases at p_{H} 7.0 and 30° shows that with some amines (e.g., $\text{C}_5\text{H}_5\text{N}$) the rate of reaction is comparable with that between (I) or (II) and SH compounds. Unlike the SH reaction, the cyclic base group reacts more rapidly with (I) than with (II). The actual formation of compounds with (I) and (II) is proved by the isolation of the following products: $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and (I) or $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}-\text{Na}_2\text{CO}_3$ -33% aq. NHMe_2 at 80° give the betaine $^+\text{NMe}_2(\text{CH}_2\cdot\text{CO}_2)^-\text{Na}^+\cdot\text{H}_2\text{O}$, and with (II) the double salt

$[^+\text{NMe}_2(\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2]^-\text{NaI}\cdot\text{H}_2\text{O}$, is formed. Nicotinic acid affords the betaine

$-\text{CO}_2\cdot\text{C}_5\text{H}_4>\text{N}^+\cdot\text{CH}_2\cdot\text{CO}_2^-\text{Na}^+\cdot 4\text{H}_2\text{O}$, and the betaine

$-\text{CO}_2\cdot\text{C}_5\text{H}_4>\text{N}^+\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, and its isomeride $(\text{NH}_2)\cdot\text{CO}\cdot\text{C}_5\text{H}_4>\text{N}^+\cdot\text{CH}_2\cdot\text{CO}_2^-$; $(\text{CH}_2)_6\text{N}_4$ gives the betaine $[(\text{CH}_2)_6\text{N}_4]^+\cdot\text{CH}_2\cdot\text{CO}_2^-\text{NaI}\cdot 3\text{H}_2\text{O}$. The prep. of the Na salt of $\alpha\alpha'$ -dicarboxymethylamine from $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}-\text{NaOH}-\text{NH}_2\text{Me}$ is described.

J. W. B.

Dissociation constants and structures of glutamic acid and its esters. A. NEUBERGER (Biochem. J., 1936, 30, 2085—2094).—*N*-Carbobenzyloxyglutamic anhydride with EtOH at 125° yields α -*Et H N*-carbobenzyloxyglutamate, m.p. 100° , which with H_2 -Pd in 80% EtOH + HCl gives α -*Et H* glutamate (I), m.p. 110° . The dissociation consts. for glutamic acid are 2.164 (first CO_2H), 4.315 (second CO_2H), and 9.96 (NH_3); for γ -*Et H* glutamate they are 2.148 (CO_2H) and 9.19 (NH_3); for (I) they are 3.847 (CO_2H) and 7.838 (NH_3); for *Et*₂ glutamate 7.035 (NH_3). F. A. A.

Synthesis of di-*N*-methylhomocystine and *N*-methylmethionine and a study of their growth-promoting ability in connexion with a cystine-deficient diet. W. I. PATTERSON, H. M. DYER, and V. DU VIGNEAUD (J. Biol. Chem., 1936, 116, 277—284).—Bromination of $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ (A., 1935, 1486) and treatment of the product with NH_2Me affords *S*-benzyl-*N*-methylhomocysteine (I), m.p. 220 — 222° (corr.), converted by Na in liquid NH_3 and subsequent oxidation into di-*N*-methylhomocystine (II), m.p. 257 — 260° (corr.). Similar reduction of (I) followed by treatment with MeI gives *N*-methylmethionine (III), m.p. 255 — 257° (corr.). Feeding experiments show that both (II) and (III) are as effective as an equiv. amount of cystine in promoting growth in rats fed on a cystine-deficient diet. J. W. B.

Nitrile esters of β -methylpropene- $\alpha\alpha\gamma\gamma$ -tetra-carboxylic acid. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1936, 11, 557—568).—Condensation of $\text{OEt}\cdot\text{CMe}\cdot\text{CR}\cdot\text{CN}$ (I) ($\text{R} = \text{CN}$ or CO_2Et) with $\text{CHNa}(\text{CO}_2\text{Et})_2$ (II) or $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ (III) and of (I) ($\text{R} = \text{CN}$) with $\text{CHNa}(\text{CN})_2$ (IV) resembles that of $\text{OEt}\cdot\text{CH}\cdot\text{CR}\cdot\text{CN}$ (A., 1930, 461), but that of (I) ($\text{R} = \text{CO}_2\text{Et}$) with (IV) takes a different course. The normal condensation

is such that the ethylenic linking takes a position remote from the C carrying the larger no. of CO_2Et . $\text{CH}(\text{OEt})_3$ and $\text{CH}_2(\text{CN})_2$ in hot H_2O give α -ethoxy-ethylidenemalononitrile (I) ($\text{R} = \text{CN}$), b.p. $120^\circ/2\text{ mm.}$, m.p. 91° , which (a) with (II) in EtOH gives the Na derivative (V), $+0.5\text{H}_2\text{O}$ (red FeCl_3 colour), of $\text{Et}_2\beta\beta$ -dicyano- α -methyl-ethylidenemalonate (VI), (b) with (III) gives the Na derivative (VII), $+ \text{H}_2\text{O}$, of $\text{Et}\alpha\gamma\gamma$ -tricyano- β -methyl- Δ^β -butenoate (VIII), and (c) with (IV) gives the Na derivative (IX), $+ \text{H}_2\text{O}$, of $\alpha\gamma\gamma$ -tetracyano- Δ^α -isobutene (X), and a substance, $\text{C}_8\text{H}_4\text{N}_4$, $+ \text{EtOH}$, m.p. 226° (formed as sole product if the reaction is effected without cooling). (V) with aq. acid gives an oil, probably (VI), which, however, readily passes into $\text{Et}\gamma$ -cyano- α -carbethoxy- γ -carbomethyl-, m.p. 232° , and α -carbethoxy- $\gamma\gamma$ -dicarbomethyl- Δ^β -butenoate, m.p. 164° . (VII) and aq. acid give (VIII), m.p. 212 – 213° (decomp.). Acid does not give a ppt. with an aq. solution of (IX), but Et_2O extracts cryst. (X) from the acidified solution. (X) is unstable alone, but stable in H_2O ; it is a strong acid. (I) ($\text{R} = \text{CO}_2\text{Et}$) with (II) gives the Na derivative, cryst., hygroscopic (red FeCl_3 colour), of $\text{Et}\alpha$ -cyano- γ -carbethoxy- β -methylglutaconate, cryst., into which it is converted by HCl ; but with (IV) it gives (VII), from which (VIII) was obtained with m.p. 227 – 228° (decomp.).

R. S. C.

Sullivan colorimetric test for guanidine. M. X. SULLIVAN (J. Biol. Chem., 1936, 116, 233–235; cf. Braun and Rees, A., 1936, 1006).—Modifications of the original procedure (cf. *ibid.*, 321) are given enabling certain guanidine derivatives to be distinguished from guanidine.

F. A. A.

Reduction of nitroguanidine. VII. Preparation of aminoguanidine by catalytic hydrogenation. E. LIEBER and G. B. L. SMITH (J. Amer. Chem. Soc., 1936, 58, 2170–2172; cf. A., 1936, 321).—Aminoguanidine [sulphate, m.p. 206° (Dennis bar)] is best prepared by reduction of nitroguanidine (I) with H_2 (125 atm.) and PtO_2 in 15% AcOH at room temp. Reduction of (I) under various conditions (catalyst, solvent, temp.) is also studied; in neutral and basic media (not acid) nitrosoguanidine is first formed.

H. B.

Oxides of thiocarbamide. I. Thiocarbamide dioxide, $(\text{NH}_2)_2\text{CSO}_2$. II. Thiocarbamide trioxide (formamidinesulphonic acid). J. BÖESEKEN (Rec. trav. chim., 1936, 55, 1040–1043, 1044–1045).—I. Contrary to statements by Barnett (J.C.S., 1910, 97, 63), the dioxide (I) formed by $\text{CS}(\text{NH}_2)_2$ and H_2O_2 is neutral and strongly reducing in alkaline solution. With KMnO_4 – H_2SO_4 (excess), HNO_3 , or FeCl_3 – HNO_3 1 O is absorbed before SO_4^{2-} is liberated; AcO_3H leads to a cryst. trioxide (II). Cryst. (I) is stable; in H_2O it slowly liberates SO_2 . It is stable in conc. H_2SO_4 at $>100^\circ$, but at 150° gives SO_2 . The following reaction is demonstrated in aq. NH_3 : $(\text{I}) + 2\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O}$. In aq. NH_3 reaction is: $(\text{I}) + 2\text{NH}_4\text{OH} \rightarrow \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_2$, the $(\text{NH}_4)_2\text{SO}_2$ acting as a strong reducing agent. Thus in aq. NH_3 (I) liberates Cd from CdO_2 , MnO_2 , and then MnO from KMnO_4 . As from $(\text{NH}_4)_2\text{AsO}_3$ etc.; with NiSO_4 – NH_3 it gives a yellow complex, converted by warming into Ni

(mirror) or by air into the Ni salt; NH_3 – Co^{++} gives a brown solution stable in air, but depositing Co and CoS when warmed. (I) is $\text{NH}_2\text{C}(\text{NH}_2)\cdot\text{SO}_2\text{H}$.

II. (II) is formamidinesulphonic acid, $\text{NH}_2\text{C}(\text{NH}_2)\cdot\text{SO}_3\text{H}$, giving with hot aq. $\text{Ba}(\text{OH})_2$, BaSO_3 and $\text{CN}\cdot\text{NH}_2$. $\text{CS}(\text{NH}_2)_2$ with HNO_3 – AcOH gives the insol. dithioformamidine nitrate; with 2 mols. of AcO_2H it gives (I), and with 3 mols. yields (II). (II) is also obtained from dithioformamidine sulphate and AcO_2H .

R. S. C.

Acidimetric determination of sodium mono-methyl- and dimethyl-arsenates. G. N. THOMIS (Praktika, 1935, 10, 130–134; Chem. Zentr., 1936, i, 1065).—66% EtOH is used as solvent and bromophenol-blue and bromocresol-purple as indicators.

H. N. R.

Cobaltammines which co-ordinate with quaternary ammonium bases.—See A., I, 42.

Werner complexes.—See A., I, 42.

Stereochemistry of complex inorganic compounds. II, III.—See A., I, 42.

Electrolysis of magnesium methyl iodide in *n*-butyl ether. W. V. EVANS and E. FIELD (J. Amer. Chem. Soc., 1936, 58, 2284–2286).—Electrolysis (method: A., 1936, 830) of MgMeI in Bu^n_2O at 143° (at which temp. polarisation is almost completely absent) using bright Pt electrodes gives CH_4 and C_2H_6 together with the following minor products (all of which are derived from the Bu^n_2O): CO_2 (variable), C_4H_{10} , Δ^α -butene, and (after hydrolysis) Bu^nOH , pentan- β -ol, and high-boiling products. The efficiency of the electrolysis is much $<$ in Et_2O (cf. *loc. cit.*). Use of a platinised anode with Et_2O – MgMeI increases the effective area, but decreases the effective c.d. by the same amount.

H. B.

Alkylation of aromatic [hydrocarbons] with olefines in presence of boron fluoride. V. N. IPATIEV and A. V. GROSSE (J. Amer. Chem. Soc., 1936, 58, 2339; cf. A., 1936, 975).— PhEt (21%) and $\text{C}_6\text{H}_4\text{Et}_2$ (3%) are obtained from C_6H_6 , C_2H_4 , BF_3 , and a little H_2O at 20 – 25° in a Ni-lined autoclave.

H. B.

Condensation of aryl methyl ketones. D. B. CLAPP and A. A. MORTON (J. Amer. Chem. Soc., 1936, 58, 2172; cf. Bernhauer *et al.*, A., 1936, 1100).—1:3:5-Tri-*p*-diphenylbenzene, m.p. 230.5 – 231° (23%), and 1:3:5-tri- α , m.p. 190.5 – 191° (18%), and - β , m.p. 234 – 235° (20%), -naphthylbenzene are prepared from *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{COMe}$ and α - and β - $\text{C}_{10}\text{H}_7\cdot\text{COMe}$, respectively, with NH_2Ph and $\text{NH}_2\text{Ph}\cdot\text{HCl}$ at 175° in CO_2 (cf. Reddelien, A., 1912, i, 363).

H. B.

Optically active quaternary ammonium salts from *d*- and *l*- β -octyl *p*-bromobenzenesulphonate and *tert*-amines. R. C. CARY, J. F. VITCHA, and R. L. SHRINER (J. Org. Chem., 1936, 1, 280–287).—*d*- and *l*-, m.p. 30° , $[\alpha]_D^{25} \pm 10^\circ$ in EtOH , and *dl*- β -Octyl *p*-bromobenzenesulphonate, m.p. 40 – 41° , readily hydrolysed by atm. H_2O , with NMe_3 – EtOH give *d*- and *l*-, m.p. 208 – 210° , $[\alpha]_D^{25} \pm 95^\circ$ in EtOH , and *dl*-trimethyloctyl- β -ammonium *p*-bromobenzenesulphonate, m.p. 204° , respectively. With $\text{C}_5\text{H}_5\text{N}$ in

Et₂O there are formed dl-β-octylpyridinium p-bromobenzenesulphonate, m.p. 111–112°, and the impure active forms of rotation opposite in sign to that of the ester used. The reaction probably occurs by simultaneous addition of NR₃ and expulsion of p-C₆H₄Br·SO₃ without actual existence of the active radical or ion in the free state. NHMe₃ and C₅H₅N p-bromobenzenesulphonate have m.p. 113–114° and 134–135°, respectively. R. S. C.

4 : 4'-Dibenzyltriphenylmethane and its derivatives as free radicals. E. CONNERADE (Bull. Soc. chim. Belg., 1936, 45, 647–666).—4 : 4'-Dibenzylbenzophenone (A., 1935, 1371) with LiPh or MgPhBr affords pp'-dibenzyltriphenylcarbinol (I), converted by HCl-EtCl at -5° into its unstable chloride (II), which with C₅H₅N at 65–70° (CO₂) affords 1-benzylidene-4-α-p-benzylphenylbenzylidene-Δ^{2:5}-cyclohexadiene, CHPh·C₆H₄·CPh·C₆H₄·CH₂Ph [also formed by loss of H₂O from (I)], oxidised by air to the internal ether, CHPh<O>CPh·C₆H₄·CH₂Ph, but reduced by Zn-AcOH-C₅H₅N (CO₂) to pp'-dibenzyltriphenylmethane. Ag does not convert (II) into a free radical, but merely catalyses HCl elimination. Oxidation of (I) with CrO₃-AcOH at 100° gives a little CO(C₆H₄Bz)₂ and (mainly) pp'-dibenzoyltriphenylcarbinol (III), amorphous and cryst., softens 85°, m.p. 95° (readily retains H₂O and MeOH), converted by HCl in C₆H₆ into its chloride, which with Ag at 50–80° (CO₂) affords pp'-dibenzoyltriphenylmethyl (peroxide, m.p. 73°); cryoscopic measurements in C₆H₆ indicate 36% of this free radical in equilibrium with its dimeride. Reduction of (III) with Na-Hg-EtOH affords pp'-di-α-hydroxybenzyltriphenylcarbinol, m.p. 55° (amorphous Ac₂ derivative), decomp. at 110° with loss of H₂O and polymerisation. With the exception of (III) none of the compounds could be obtained cryst. and all are halochromic with H₂SO₄.

J. W. B.

Reaction of potassamide in liquid ammonia with β-bromo-α-diarylethylenes. G. H. COLEMAN, W. H. HOLST, and R. D. MAXWELL (J. Amer. Chem. Soc., 1936, 58, 2310–2312).—β-Bromo-α-diarylethylenes, like the Cl-analogues (A., 1934, 287), are converted by KNH₂ in liquid NH₃ into tolanes. The probable mechanism is: CAR₂·CHBr → Br⁻ + CAR₂⁺·CH → ⁺CAR·CHAr → CAR:CAR + H⁺. Thus, β-bromo-α-di-o-, b.p. 150–155°/1.5 mm., and -m-, b.p. 186–191°/10 mm., -tolyl- and -di-o-, m.p. 101.6–102.6°, and -m-, b.p. 225–230°/6 mm., -anisyl-ethylenes, prepared from the appropriate CAR₂·CH₂ (from CHAr₂·CH₂Cl and EtOH-KOH or C₂H₅N) and Br in CCl₄, give 2 : 2' (I), b.p. 138–142°/0.75 mm., and 3 : 3' (II), m.p. 73.5–74°, -dimethyl- and 2 : 2', m.p. 124.5–125°, and 3 : 3', m.p. 63–63.5°, -dimethoxy-tolane, respectively. (I) and (II) are also obtained from αβ-dibromo-αβ-di-o-, m.p. 171–172°, and -m-, m.p. 166.5–167°, -tolylethane, respectively, and EtOH-KOH. CHAr₂·CHBr₂ [from CHBr₂·CH(OEt)₂ and ArH in conc. H₂SO₄ at >50°] and CHAr₂·CHCl₂ (cf. loc. cit.) are similarly converted into tolanes; the di-p-ethylphenyl derivatives give smaller yields than the di-phenyl and -p-tolyl analogues. All the tolanes are reduced (Na, EtOH) to the corresponding di-

** (A., II.)

benzyls; 4 : 4'-diethyl- and 3 : 5 : 3' : 5'-tetramethyl-dibenzyl have m.p. 69.8–70.2° and 86–86.6°, respectively. All b.p. and m.p. are corr. H. B.

Isolation of αβ-diketones from ozonisation of disubstituted acetylenes. T. L. JACOBS (J. Amer. Chem. Soc., 1936, 58, 2272–2273; cf. Hurd and Christ, A., 1936, 1359).—(CPh)₂ and O₃ in light petroleum at 5–15°, followed by steam distillation, give BzOH (65.5%) and benzil (5.5%); the ozonide (obtained at -78°) decomposes at room temp. to a black tar. The ozonide from CPh:C·CH₂Ph (in EtCl at -40° to -30°) with aq. KI gives 25% of Ph benzyl diketone and tar; decomp. with hot H₂O affords BzOH (60%), CH₂Ph·CO₂H (10%), and tar.

H. B.

Synthesis and properties of spirans from phenylpropyl-cyclanols [-cycloalkanols]. D. PERLMAN, D. DAVIDSON, and M. T. BOGERT (J. Org. Chem., 1936, 1, 300–304).—The Grignard reagent from Ph·[CH₂]₃·Br, b.p. 120–122°/20 mm., and cyclohexanone give 1-γ-phenylpropylcyclohexanol, b.p. 139–140°/3–4 mm. (phenylurethane, m.p. 106–106.5°), which is dehydrated when distilled at 5 mm., and with 85% H₂SO₄ gives 93% of 1 : 1-pentamethylene-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 40–41°, b.p. 153–154°/10 mm.; this with Se gives only a fluorescent oil (no picrate) and with KMnO₄-H₂O₂ affords αα-pentamethylenehomophthalic acid, m.p. 154.5–155.5° (bath preheated to 145°) with formation of a liquid anhydride. cyclopentanone affords similarly 1-γ-phenylpropylcyclopentanol, b.p. 136–137°/2–3 mm. (phenylurethane, m.p. 90–91°), and thence 1 : 1-tetramethylene-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 137–138°/10 mm., which with Se gives a fluorescent oil and with KMnO₄-H₂O₂ or CrO₃ αα-tetramethylenehomophthalic acid, m.p. 130–130.5°.

R. S. C.

Synthesis of phenanthrenes from hydroxy-derivatives of β-phenylethylcyclohexanes. Nature of the by-product. D. PERLMAN, D. DAVIDSON, and M. T. BOGERT (J. Org. Chem., 1936, 1, 288–299).—The spiran nature of the by-product in this type of synthesis is demonstrated. PhCHO (0.55 mol.) and the Grignard reagent from cyclohexylmethyl bromide (prep. by PBr₃), b.p. 82–83°/26 mm., give β-cyclohexyl-α-phenylethyl alcohol, m.p. 54–56°, b.p. 142–143°/3 mm. (phenylurethane, m.p. 91–92°), which with 90% H₂SO₄ gives a thermoplastic, resinous polyimide of the derived olefine. The Grignard reagent from cyclohexyl chloride (modified prep.) with CH₂Ph·CHO gives α-cyclohexyl-β-phenylethyl alcohol, m.p. 57.5°, b.p. 139–143°/2 mm. (phenylurethane, m.p. 83.5–84.5°), which with 90% H₂SO₄ affords 65% of a mixture (I), b.p. 135–150°/10 mm., n_D²⁰ 1.5486, and a small amount of a polyimide, b.p. 220°/2 mm. (? of the derived olefine). 1-β-Phenylethylcyclohexanol (prep. from cyclohexanone and MgBr·CH₂·CH₂Ph), m.p. 57°, b.p. 145°/2–3 mm. (phenylurethane, m.p. 125–126°), with 50 or 85% H₂SO₄ or by distillation with a trace of I gives 90% of a mixture, b.p. 135–137°/10 mm., which, when fractionated, gives 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (II), b.p. 146–147°/10 mm., [giving with Se at 290–320° 91% of phenanthrene

(III)], and impure 1:1-pentamethylene-2:3-dihydroindene (IV), b.p. 135.5—137.5°/10 mm. By calculation from *n* (I), which gives 81% of (III), is believed to contain 85.4% of (II) and 14.6% of (IV). 1- β -Phenylethyl-2-methylcyclohexanol (prep. from 2-methylcyclohexanone and $\text{MgBr}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$), b.p. 150—151°/5—6 mm. (phenylurethane, m.p. 132—133°), with 85% H_2SO_4 gives no spiran, but 92% of 12-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 145—147°/10 mm., which gives 89% of (III) or with $\text{KMnO}_4\text{--H}_2\text{O}_2$ $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$. With $\text{KMnO}_4\text{--H}_2\text{O}_2$ (II) gives only $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, but (IV) gives also $\alpha\alpha$ -pentamethylenehomophthalic acid, m.p. 154.5—155.5°, which proves the nature of (IV). These and reactions described in the lit. are evidence that dehydration precedes cyclisation. R. S. C.

Phenanthrene derivatives. VI. Preparation of 1-, 2-, and 3-halogenophenanthrenes. W. E. BACHMANN and C. H. BOATNER (J. Amer. Chem. Soc., 1936, 58, 2194—2195).—Partly a more detailed account of work previously reviewed (A., 1936, 836). Phenanthrene-1-, -2-, and -3-diazonium sulphates, prepared by de Milt and Van Zandt's method (A., 1936, 1502), are converted by Schwechten's procedure (A., 1932, 1244) into 1-, m.p. 120—120.5°, and 2-, m.p. 85.5—86°, -chloro-, 3-chloro-, m.p. 80.5—81.5°, and 1-, m.p. 109.5—110°, 2-, m.p. 95—96°, and 3-, m.p. 83—84°, -bromo-phenanthrene, respectively. Treatment with KI gives 1-, m.p. 112.5—113°, 2-, m.p. 116—116.5°, and 3-, m.p. 83.5—84°, -iodophenanthrene, respectively. The corresponding phenanthrols are also prepared. H. B.

Effect of catalysts on the phenanthrene-bromine reaction. C. C. PRICE (J. Amer. Chem. Soc., 1936, 58, 2101—2104).—The rate of addition of Br to phenanthrene in CCl_4 at 25° (cf. A., 1936, 1498) is accelerated by SbCl_5 (0.1 equiv.) and retarded by I (0.05—0.1 equiv.) (probably owing to interruption of the chain mechanism). I (1/15 equiv.) catalyses the substitution reaction (*loc. cit.*), but does not effect elimination of HBr from 9:10-dibromo-9:10-dihydrophenanthrene except in presence of an equiv. amount of Br. The results cannot be reconciled with the addition-elimination theory of aromatic substitution; a reaction similar to that proposed by Pfeiffer and Wizinger (A., 1928, 633) is probable. Recalculation of Bruner's data (cf. A., 1902, ii, 447) for the rate of bromination of C_6H_6 in presence of I indicates that the catalyst is BrI_3 . H. B.

Reduction of aromatic nitro-compounds. II. V. O. LUKASCHEVITSCH (J. Gen. Chem. Russ., 1936, 6, 1064—1073).—Azo- and azoxy-compounds are converted quantitatively into hydrazo-compounds by Zn and aq. NaOH at 68—72°, but when arylhydroxylamines or NO_2 -compounds are present all substrates are reduced to amines under the same conditions. It is concluded that hydrazo-compounds are not intermediate products in the reduction of NO_2 -compounds, but that these, together with azoxy- and azo-compounds, are reduced directly to amines. R. T.

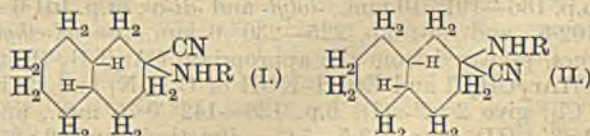
Application of the electronic theory in organic chemistry. VIII. Electroisomerism of *o*-toluidine and its derivatives. A. M. BERKENGEM

and R. S. LIVSCHITZ (J. Gen. Chem. Russ., 1936, 6, 1025—1038).—*o*-Acet-toluidide (I) and $\text{HNO}_3\text{--H}_2\text{SO}_4$ at -5° yield a mixture of 4- (79%) and 5-nitro-*o*-acet-toluidide (19%), the constitution of which is established by conversion into the corresponding nitroanthranilic acids and nitroanilines. The conclusion is that (I) exists as a mixture of two electronic isomerides. R. T.

Alkyl hypochlorites. Action on Schiff's bases. II. C. MUSANTE and R. FUSCO (Gazzetta, 1936, 66, 639—648; cf. A., 1936, 964).— $\text{CMe}_2\text{Et}\cdot\text{OCl}$ (I) and $\text{NR}\cdot\text{CHPh}$ give PhCHO and a chlorinated arylamine; when $\text{R} = p\text{-C}_6\text{H}_4\cdot\text{OMe}$, an amidine is also obtained. Thus when $\text{R} = o\text{-}$ and $m\text{-C}_6\text{H}_4\text{Me}$, the respective products are 5-chloro-*o*- and 6-chloro-*m*-toluidine. Since PhCHO and (I) form BzCl , a benzamide may be obtained. Thus 1:5:2- $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{N}\cdot\text{CHPh}$ yields 1:5:2- $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{NHBz}$; 1:4:2- $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{N}\cdot\text{CHPh}$, however, gives 1:4:5:2- $\text{C}_6\text{H}_2\text{MeCl}_2\cdot\text{NH}_2$. 1:4:2- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{N}\cdot\text{CHPh}$ is chlorinated to 1:4:5:2- $\text{C}_6\text{H}_2\text{Me}_2\text{Cl}\cdot\text{NH}_2$, and $o\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CHPh}$ to 2:5:1- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{OMe}$; $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CHPh}$ yields, however, 2:3:5- (or 2:3:6-) trichloro-*p*-anisidine, m.p. 112° (hydrochloride; oxidised to trichlorobenzquinone), and $\text{NN}'\text{-di-}p\text{-anisylbenzamidine}$, m.p. 126°, synthesised by treating benz-*p*-anisidide with PCl_5 to obtain *N-p-anisylbenzimidochloride*, m.p. 52—62°, which is then treated with *p*-anisidine. $o\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CHPh}$ gives a dichlorophenetidine, m.p. 48°, and $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CHPh}$ a trichloro-*p*-phenetidine, m.p. 89° (with no amidine). E. W. W.

Quaternary ammonium iodides of dimethyl-*p*-toluidine. M. Q. DOJA (J. Indian Chem. Soc., 1936, 13, 527—530).—*p*-Tolyl dimethyl-ethyl-, m.p. 196°, -*n*-propyl-, m.p. 200°, -*n*-butyl-, m.p. 201—202°, -*n*-amyl-, m.p. 199—201°, and -allyl-, m.p. 197°, and phenyldimethyl-*n*-amyl-ammonium iodide, m.p. 205°, are prepared; all sublime at about their m.p. when heated in an open tube. E. W. W.

Isomeric 2-arylamino-2-cyano-trans-decahydronaphthalenes, and the condensation of the cyanohydrin of 3-methylcyclopentanone with aniline. R. D. DESAI, R. F. HUNTER, and M. HUSSAIN (J.C.S., 1936, 1675—1676).—Condensation of the cyanohydrin of *trans*- β -decalone with arylamines gives pairs of isomerides, separated by crystallisation, corresponding with (I) and (II), hydrolysed to the corresponding 2-carboxylamides. The two m.p. given



after the following corresponds, respectively, with the A and B forms: 2-anilino-2-cyano-, m.p. 135° and 120° (corresponding -2-carboxylamide, m.p. 158° and 141°; A form of corresponding -2-carboxylic acid, m.p. 198°), 2-*p*-bromoanilino-2-cyano-, m.p. 132° and 141° (corresponding -2-carboxylamide, m.p. 180° and 171°), 2-*o*-toluidino-2-cyano-, m.p. 100° and 111° [corresponding -2-carboxylamide (A form), m.p. 157°], 2-*m*-toluidino-2-cyano-, m.p. 126—127° and 123—124° [corresponding -2-carboxylamide (A form), m.p.

122°], 2- β -naphthylamino-2-cyano-, m.p. 162° and 160° (corresponding -2-carboxylamide, m.p. 238° and 221°), -trans-decahydronaphthalene. Only one form of the following was isolated: 2-p-toluidino-2-cyano-, m.p. 130° (corresponding -2-carboxylamide, m.p. 166—167°), and 2- α -naphthylamino-2-cyano-, m.p. 133° (corresponding -2-carboxylamide, m.p. 174°), -trans-decahydronaphthalene. Only one form was isolated of 1-anilino-1-cyano-3-methylcyclopentane, m.p. 49° (corresponding -1-carboxylamide, m.p. 158—159°), prepared from 3-methylcyclopentanone, KCN, NH_2Ph , and AcOH. H. G. M.

Acylation of aromatic aminosulphonic acids. II. Reiterated acylation method. N. N. VOROSCHCOV and A. I. TITOV (J. Appl. Chem. Russ., 1936, 9, 1852—1857).—1:6- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ is easily acetylated in boiling AcOH containing NaOAc; the filtrate, instead of pure AcOH, may be used as solvent for other acetylations. HCO_2H (80%) containing HCO_2Na reacts similarly. J. J. B.

Molecular rearrangement of triphenylmethylalkoxyamines. W. S. GUTHMANN and J. STIEGLITZ (J. Org. Chem., 1936, 1, 31—37).—Triphenylmethylhydroxylamine *O*-ethers or their hydrochlorides rearrange, when heated alone or with various reagents, the products being (a) COPh_2 and NH_2Ph , (b) $\text{CPh}_3\cdot\text{OH}$ and a hydroxylamine *O*-ether, or (c) CPh_3Cl and the hydroxylamine *O*-ether hydrochloride. The rearrangement is due to electron deficiency of the N-O linking, but must be initiated by a reagent or circumstances promoting the formation of univalent N compounds. Thus, reaction (a) is due to dissociation to the appropriate alcohol and the radical $\text{CPh}_3\cdot\text{N}<$; this radical rearranges to benzophenoneanil, which yields the final reaction products by hydrolysis. Reaction (b) is due to direct hydrolytic fission of the C-N linking. Reaction (c) is caused by fission of 1 mol. of the ether at the C-N linking by 2 mols. of HCl. Two or more of the reactions may occur simultaneously. The ease of rearrangement of the ethers is $\text{CH}_2\text{Ph} > \text{Me}$, both $>$ triphenylmethylhydroxylamine itself. CPh_3Cl and $\text{NH}_2\cdot\text{OMe}$ in C_6H_6 give triphenylmethylhydroxylamine *O*-Me ether, m.p. 91.5—91.6° [hydrochloride (I), m.p. 179—180° (decomp.)], loses HCl in vac. and dissociates in Et_2O into CPh_3Cl and $\text{NH}_2\cdot\text{OMe}\cdot\text{HCl}$, which is stable to heat and reagents in Et_2O , but in CCl_4 alone or with PCl_5 gives COPh_2 . (I) with P_2O_5 gives $\text{CPh}_3\cdot\text{OH}$. CPh_3Cl and $\text{NH}_2\cdot\text{OCH}_2\text{Ph}$ in C_6H_6 give triphenylmethylhydroxylamine *O*- CH_2Ph ether (II), m.p. 118° [hydrochloride (III), softens at 152°, m.p. 180—190° (decomp.), unstable]. (I) or (III) with PCl_5 in hot CCl_4 or with P_2O_5 at 160° gives COPh_2 , or with PCl_5 alone at 160° gives COPh_2 and NH_2Ph ; (III) with P_2O_5 or (I) alone or with P_2O_5 at 445° gives NH_2Ph , COPh_2 , and a little PhCHO . In all cases $\text{CPh}_3\cdot\text{OH}$ was also formed. R. S. C.

Nitro- and amino-compounds of substituted benzotrifluorides.—See B., 1936, 1143.

Manufacture of aryl aminoalkyl sulphones.—See B., 1936, 1196.

Reaction between 1-bromo- β -naphthol and benzenediazonium salts. J. S. JOFFE (J. Gen.

Chem. Russ., 1936, 6, 1074—1078).—In aq. NaOH 1:2- $\text{C}_{10}\text{H}_6\cdot\text{Br}\cdot\text{OH}$ and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OH}$ give low yields of impure 1- p -nitrobenzeneazo- β -naphthol, which is obtained in 96% yield, and of high purity, when $\text{Na}_2\text{S}_2\text{O}_3$ is present. The results are ascribed to formation of NaOBr, which reacts with the substrates to yield different by-products, and is removed by $\text{Na}_2\text{S}_2\text{O}_3$. R. T.

Hydrogen sulphite compounds of azo-dyes. V. Hydrogen sulphite reaction of azo-dyes containing two auxochromes. N. N. VOROSCHCOV and A. TSHERKASSKI (J. Amer. Chem. Soc., 1936, 58, 2327—2333).—Contrary to King (A., 1932, 609), monoazo-dyes containing 2 OH can give additive compounds with 2 mols. of NaHSO_3 , thus proving the dominant importance of the auxochrome group and disproving Spiegel's theory. King's failure to obtain a similar additive compound is due to the use of a compound (2:2'-dihydroxy-1:1'-azonaphthalene-4-sulphonic acid) in which one of the OH is inactivated (by the $m\text{-SO}_3\text{H}$).

The NaHSO_3 compound of 1:8- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ (A., 1916, i, 293) gives a stable diazonium chloride (I), which with $\text{EtOH}\text{-}\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ at $>12^\circ$ affords the aminoazo-dye, $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\cdot\text{NaHSO}_3$ (II). $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$ and (I) in $\text{AcOH}\text{-NaOAc}$ give the hydroxyazo-dye, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\cdot\text{NaHSO}_3$ (III), whilst in aq. NaOH 4:8'-dihydroxy-1:1'-azonaphthalene (IV) (Na salt) results. (II) and 35% NaHSO_3 at room temp. afford the dye, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\cdot 2\text{NaHSO}_3$ (V); the original NH_2 is hydrolysed. (V) is also obtained from (III) and 35% NaHSO_3 at 70° and from (IV) (in an impure condition). Hydrolysis of (V) with aq. Na_2CO_3 at 40° gives (III), whilst (V) and (III) with warm 25% NaOH afford (IV). Alternative structures for (II), (III), and (V) are discussed. The present position of views regarding the structure of the NaHSO_3 compounds of azo-dyes is summarised (cf. Bogdanov, A., 1932, 842). H. B.

Action of diazonium salts on trichloro- α -nitro- β -acetoxyparaffins. F. D. CHATTAWAY, J. G. N. DREWITT, and G. D. PARKES (J.C.S., 1936, 1693—1694).— $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CCl}_3$ and diazotised NH_2Ph in $\text{EtOH}\text{-HCl}\text{-H}_2\text{O}$ give $\gamma\gamma\gamma$ -trichloro- α -nitro- β -acetoxypropionalphenylhydrazones, m.p. 137°. The corresponding *o*-, labile form, m.p. 109°, stable form, m.p. 115°, *m*-, m.p. 127°, and *p*-, labile and stable forms, m.p. 152°, -tolyl-, *p*-chlorophenyl-, m.p. 165°, 2:4-dichlorophenyl-, m.p. 155°, and *p*-nitrophenyl- (I), labile form, m.p. 187°, stable form, m.p. 189°, -hydrazones were similarly prepared. $\gamma\gamma\delta$ -Trichloro- α -nitro- β -acetoxypentanalphenylhydrazone has m.p. 152°; the corresponding *p*-tolyl-, m.p. 166°, *p*-chlorophenyl-, m.p. 177°, and *p*-nitrophenyl-, stable form, m.p. 187°, -hydrazone. $\gamma\gamma\gamma$ -Trichloro- α -nitro- β -hydroxypropane with PhN_2Cl in EtOH gives nitroformazyl, also obtained from PhN_2Cl and MeNO_2 , and with $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{Cl}$ gives *pp'*-dichloronitroformazyl, m.p. 188°, and a trace of $\gamma\gamma\gamma$ -trichloro- α -nitro- β -hydroxypropanal-*p*-chlorophenylhydrazone, m.p. 160°. *Bis*-2:4-dichloronitroformazyl, similarly prepared, has m.p. 189°. Amines react with the foregoing hydr-

azone acetic esters to give a substituted amine; thus (I) and *p*-C₆H₄Me·NH₂ in EtOH (water-bath; 12 hr.) give $\gamma\gamma\gamma$ -trichloro- α -nitro- β -*p*-toluidinopropanal-*p*-nitrophenylhydrazone, m.p. 189° (decomp.). The corresponding *phenyl*, m.p. 164° (decomp.), *o*-tolyl, m.p. 127°, and *p*-chlorophenyl, m.p. 164°, -hydrazones were similarly prepared. $\gamma\gamma\delta$ -Trichloro- α -nitro- β -*p*-toluidinopentanalphenylhydrazone has m.p. 178° (decomp.), and $\gamma\gamma\gamma$ -trichloro- α -nitro- β -methylaminopropanalphenylhydrazone, m.p. 104° [hydrochloride, m.p. 189° (decomp.)].
H. G. M.

Direct introduction of deuterium into the aromatic nucleus. I. Qualitative comparison of the efficiencies of some acidic deuterating agents and of the influence of some aromatic substituents. C. K. INGOLD, C. G. RAISIN, and C. L. WILSON (J.C.S., 1936, 1637—1643).—The relative rates of deuteration of PhX (X = O⁻, NMe₂, OMe, H, SO₃H) and the efficiencies of the acidic reagents, H₂SO₄, H₂SeO₄, H₃O⁺, PhOH, and H₂O, containing some of the corresponding D compound, have been qualitatively evaluated, and decrease in the orders given, respectively, for aromatic substituents and reagents. No deuteration was observed with HNO₃, although nitration took place. The above orders are in agreement with the requirements of an ordinary electrophilic aromatic substitution (cf. A., 1929, 1289), and support the view that deuteration by acidic reagents is also such a substitution (cf. A., 1935, 74; 1936, 1322).
H. G. M.

Hydrolysis of arylsulphuric acids. III, IV.—See A., I, 36.

Determination of free and conjugated phenols.—See A., III, 3.

Preparation of the 3-halogeno-4-nitrophenols. H. H. HODGSON and J. H. CROOK (J.C.S., 1936, 1677—1678).—3-Halogenophenyl 3-nitrobenzenesulphonates (instead of the free phenol) with excess of HNO₃ (*d* 1.5) between -5° and -10° give the 3-halogeno-4-nitrophenyl ester in good yield (about 72%) and some of the -6-NO₂-ester, and with HNO₃-H₂SO₄ at room temp. give the -4:6-(NO₂)₂-ester. The 3-iodophenyl ester, however, is nitrated only in the 4-position. Hydrolysis of the nitrated esters with NaOH-EtOH-H₂O at 25° gives the corresponding halogenonitrophenols without displacement of the halogen. The prep. of the following 3-nitrobenzenesulphonates is described: *Ph*, m.p. 91—92° [2-, m.p. 88—89°, 3-, m.p. 110.5—111.5°, and 4-, m.p. 131—132.5°, -NO₂-derivatives]; 2:4-(NO₂)₂-derivative, m.p. 122—123°; 3-fluorophenyl, m.p. 90—91° [4-, m.p. 113—114°, and 6-NO₂-, m.p. 72—72.5°, and 4:6-(NO₂)₂-, m.p. 148—149.5°, derivatives]; 3-chlorophenyl, m.p. 111—112° [4-, m.p. 104—105°, and 6-NO₂-, m.p. 99.5—100.5°, and 4:6-(NO₂)₂-, m.p. 127—127.5°, derivatives]; 3-bromophenyl, m.p. 135—136° [4-, m.p. 109—110°, and 6-NO₂-, m.p. 110—110.5°, and 4:6-(NO₂)₂-, m.p. 137—138.5°, derivatives]; 3-iodophenyl, m.p. 143—144° (4-, m.p. 135—136°, and 6-, m.p. 130—131°, -NO₂-derivatives).
H. G. M.

Thymol derivatives of possible medicinal value. F. A. GILFILLAN and J. R. MERRITT (J. Amer. Pharm. Assoc., 1936, 25, 860—861).—Nitroso-thymol was prepared by a modified Klages method (A., 1900, i, 42) and aminothymol (Ac₂ derivative, m.p. 123°) by the Liebermann-Illinski method (A., 1886, 239).
F. O. H.

Effect of halogen substituents on rearrangement of aryl allyl ethers. II. Ethers which behave abnormally. C. D. HURD and C. N. WEBB (J. Amer. Chem. Soc., 1936, 58, 2190—2193; cf. A., 1936, 980)—2:4:6-Tribromophenyl allyl ether heated in tetrahydronaphthalene (I) gives 68% of 4:6-dibromo-2-allylphenol (II) and some 4:6-dibromo-1-methylcoumarone, b.p. 130—135°/1 mm. [also obtained from (II) and aq. AcOH-HBr (cf. Claisen and Tietze, A., 1925, i, 389)]; in absence of (I), a little *s*-C₆H₂Br₃·OH was the only identifiable product. 2:6-Dibromophenyl allyl ether in (I) similarly affords 6-bromo-2-allyl- and 2:6-dibromo-4-allylphenol, whilst 6-bromo-2-methylphenyl allyl ether, b.p. 81—85°/0.5 mm., yields 23% of 6-bromo-2-methyl-4-allylphenol, b.p. 101—110°/1.5 mm. *Ph* β -chloroallyl ether, b.p. 89—91°/12 mm., at 216—223° (no solvent) affords *o*- β -chloroallylphenol, b.p. 130—134°/12 mm. (which when heated further polymerises), and 1-methylcoumarone. Varying amounts of phenolic and neutral products are also formed in most of the above cases. Definite products could not be isolated from 4:6-dibromo-2-methylphenyl allyl, b.p. 137—141°/4 mm., m.p. 34—37°, *Ph* γ -chloroallyl (III), *Ph* γ -bromoallyl, b.p. 101—103°/7 mm., *Ph* β -bromoallyl (*o*- β -bromoallylphenol not isolable; cf. von Braun *et al.*, A., 1926, 1231), and *p*-tolyl γ -chloroallyl ethers. *o*- γ -Chloroallylphenol, b.p. 151—156°/31 mm. [obtained with (III) from PhONa and $\alpha\gamma$ -dichloropropene in C₆H₆], heated alone gives some 1-chloromethylcoumaran, b.p. 106—108°/9 mm., also obtained by the action of aq. AcOH-HBr. $\beta\gamma$ -Dichloropropene, b.p. 93—96°, is obtained in 80% yield from trichloropropane and solid NaOH. The above ethers are prepared as previously described (*loc. cit.*).
H. B.

Action of bromine in methyl-alcoholic solution on phenanthrene; new route to 9-phenanthrol and 9-phenanthrylamines. L. F. FIESER, R. P. JACOBSEN, and C. C. PRICE (J. Amer. Chem. Soc., 1936, 58, 2163—2166).—Phenanthrene (I) (in MeOH + anhyd. NaOAc) is treated with MeOH-Br and the mixture cooled to -5°, when 71—74% of an unstable 1:1 compound (II), m.p. 107.5—108° (decomp.), of 9:10-dibromo- and 9-bromo-10-methoxy-9:10-dihydrophenanthrene separates. (II) with MeOH-KOH + KOAc gives a mixture (A) (not readily separable) of approx. equal parts of (I) and 9-methoxyphenanthrene, m.p. 93—94°. (A) with 48% HBr in AcOH affords 9-phenanthrol (III) [28—30% on (I) used]. 9-Aminophenanthrene (IV), m.p. 137.5—138.5°, is obtained in 90% yield from (III) and 40—45% (NH₄)₂SO₃ in conc. aq. NH₃ at 135—140°/20—25 hr., whilst (III) and the appropriate NH₂Alk in aq. NaHSO₃ at 135—140° give 62—70% of *N*-methyl-, m.p. 88.5—89.5°, -ethyl-, m.p. 97—98°, -*n*-propyl-, m.p. 109.5—110.5°, and -*n*-butyl-, m.p. 102—103°, -9-aminophenanthrene. 9- β -Hydroxyethylaminophen-

anthrene, m.p. 101—102°, is prepared in 10% yield from (IV) and $(\text{CH}_2)_2\text{O}$ in C_6H_6 at 100°. H. B.

Hydrolytic instability of the carbon-to-carbon linking. M. S. KHARASCH and J. PORSCHKE (J. Org. Chem., 1936, 1, 265—274).—The following results are held to prove that substitution by electro-negative groups decreases the strength of the C-C linking, but that this decrease is chemically perceptible only when the total effect of the substitution exceeds a definite amount. 1-Benzyl- β -naphthol, 9-substituted 1:2:7:8-dibenzoxanthenes, and nuclear CPh_3 derivatives of PhOH , resorcinol and its Me_2 ether, and $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ are unchanged by hot 2% HCl-AcOH . However, 1:1'-arylidenebis- β -naphthols (and some aralkylidene- and alkylidene- β -naphthols) with hot 2% HCl-AcOH are partly (A) hydrolysed to RCHO and $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ and partly (B) dehydrated to 1:2:7:8-dibenzoxanthenes, and (C) with 2:5-dichlorobenzene-*anti*-diazotate (I) give, by fission, RCHO and 1-2':5'-dichlorobenzeneazo- β -naphthol. Similarly, the arylidenebis- β -naphthol Me ethers are hydrolysed (A) by 2% HCl-AcOH to RCHO and 2- $\text{C}_{10}\text{H}_7\text{-OMe}$. The extent of these fissions, particularly of the Me ethers, follows approx. the degree of negativity of the substituent R. The following are described, the naphthol derivatives being prepared by condensation with the appropriate aldehyde (unless otherwise stated) and the Me_2 ethers therefrom by Me_2SO_4 (the % fission is indicated in parentheses for each reaction): 1:1'-*p*-dimethylaminobenzylidene-, m.p. 175—176° (decomp.) (A 15; C ? 100), -*p*-anisylidene-, m.p. 190—192° (decomp.) (A 35; C 80) [Me_2 ether, m.p. 194—195° (A 45)], -benzylidene-, m.p. 203—204° (decomp.) (A 50; B 20; C 48) [Me_2 ether, m.p. 170—171° (A 45)], -o-, m.p. 205—207° (decomp.) (A 5; B 5; C 0) [Me_2 ether, m.p. 196—197° (lit. 191°) (A trace)], and -*m*-nitrobenzylidene-, m.p. 182—183° (decomp.) (A 30; B 10; C 49) [Me_2 ether, m.p. 172—173° (lit. 216°) (A 49)], - γ -phenylpropylidene- (from γ -phenyl-*n*-propylidene- γ -phenyl- α -2-hydroxy-1-naphthylpropylamine and $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ in C_6H_6 at 90—100°), m.p. 172—173° (A 35; C 64) [Me_2 ether, m.p. 146—147° (A 35)], -methylene- (A 5; B 15; C 47) [Me_2 ether, m.p. 146—147° (lit. 144—145°) (A 5)], and -trichloromethylene- [Me_2 ether (A 0) -*bis*-2-naphthol; 9- β -phenylethyl-1:2:7:8-dibenzoxanthen-, m.p. 173°. (I) and the supposed 1-triphenylmethyl-2-naphthol give the *dye*, m.p. 265—273°, which throws doubt on the structure of the naphthol. R. S. C.

Decomposition of phenolic ethers. IV. Decomposition of piperonylic acid with calcium oxide or barium hydroxide. V. Decomposition of the methylenedioxy-group with oxygen. Oxidation of the propyl group with oxygen in the liquid phase. VI. Scission of the methylenedioxy-group of dihydrosafrole. K. ONO and M. IMOTO (J. Chem. Soc. Japan, 1935, 56, 715—721, 873—877, 878—882).—IV. At 230°/40 atm. >50% of protocatechuic acid is produced, with a little pyrocatechol.

V. Dihydrosafrole, heated at 130° with a trace of MnO_2 in a stream of O_2 , yields piperonylic acid, heliotropin, and some phenols. Veratrole similarly affords veratric acid and veratraldehyde.

VI. With AlCl_3 or ZnCl_2 , dihydrosafrole yields propylpyrocatechol, and with PCl_5 , dihydrosafrole dichloride. CH. ABS. (r)

Bromination of 2:7-dihydroxynaphthalene. J. S. JOFFE and N. M. FEDOROVA (J. Gen. Chem. Russ., 1936, 6, 1079—1084).—2:7- $\text{C}_{10}\text{H}_6(\text{OH})_2$ in AcOH and Br at 5° yield 3-bromo-2:7-dihydroxynaphthalene, m.p. 135° (1:8-di-*p*-nitrobenzeneazo-derivative, m.p. 177—187°), whilst at 100° the 3:6- Br_2 -derivative (I), m.p. 144—146°, is obtained [erroneously identified as the 1:8-derivative by Scholl (A., 1922, i, 650)]. (I) or 1:3:6-tribromo-2:7-dihydroxynaphthalene (II), m.p. 205° [8-(4-sulphonaphthaleneazo)-derivative], prepared similarly to (I), and $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-N}_2\text{Cl}$ give 3:6-dibromo-2:7-dihydroxy-1:8-di-*p*-nitrobenzeneazonaphthalene, m.p. 250° (decomp.). Tetrabromo-2:7-dihydroxynaphthalene, m.p. 203—204°, is prepared as above at 100° in presence of AlCl_3 . R. T.

Chlorodihydroxyalkylbenzenes.—See B., 1936, 1196.

Aralkyl [benzyl] trithiocarbonates.—See B., 1936, 1197.

Tricyclohexylmethane series. II. Phenyl-cyclohexyl-substituted pinacols and pinacolins. O. NEUNHOEFFER and F. NERDEL (Annalen, 1936, 526, 47—58).—Restrictions of reactions caused by the cyclohexyl group are very marked and occur with all types of change. The effect cannot be ascribed entirely to steric hindrance, even if it is admitted that the residue makes an unusual space demand as a consequence of the incompletely rigid arrangement of its C atoms which do not lie in one plane.

Contrary to Gauerke *et al.* (A., 1928, 635), $\text{Mg cyclohexyl chloride}$ (I) behaves only as a reducing agent towards benzil, yielding hydrobenzoin. With $\text{Et}_2\text{C}_2\text{O}_4$ the reagent gives hydroxycyclohexylacetic acid, b.p. 90—100°/0.5 mm. (hydrazide, m.p. 199°), Et hydroxycyclohexylacetate (II), b.p. 123—123.5°/0.5 mm., m.p. 70°, and $\alpha\beta$ -tricyclohexylethan- α -ol- β -one, m.p. 154° [Gauerke's tetracyclohexylethylene glycol (III)]. If $\text{Me}_2\text{C}_2\text{O}_4$ is substituted for $\text{Et}_2\text{C}_2\text{O}_4$ the isolation of a small amount of tricyclohexylethylene glycol is possible, and when very large quantities of reactants are used, a minimal amount of a compound, m.p. 185°, possibly the true (III). (I) and $\text{CHPh}_2\text{-CO}_2\text{Et}$ do not interact. (II) does not lose H_2O when melted with KHSO_4 or ZnCl_2 or when distilled in presence or absence of I. Hydrogenation (PtO_2 in EtOH) of $\text{CHPh}_2\text{-CO}_2\text{Et}$ leads to Et dicyclohexylacetate, m.p. 88°, which does not react with (I) or with MgPhCl in Et_2O . It does not appear to be hydrolysed by acid or alkali, whereas $\text{CHPh}_2\text{-CO}_2\text{Me}$ after a long period of resistance is rapidly hydrolysed by aq. KOH , the incidence of the reaction appearing to depend on the production of a catalyst on the walls of the vessel. On the other hand, (II) is readily hydrolysed. Dicyclohexylacetic acid, m.p. 142°, is obtained by the slow hydrogenation of $\text{CHPh}_2\text{-CO}_2\text{H}$, unchanged material being removed by esterification with HCl-MeOH . Treatment of Na phenyldicyclohexylmethyl with BzCl or PhCN in C_6H_6 gives dimeric phenyldicyclohexylmethyl, m.p. 207°, and

triphenyltriazine, m.p. 230°, respectively. Unexpectedly $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{Me}$ and (I) afford $\alpha\alpha$ -diphenyl- β -cyclohexylethan- α -ol- β -one, m.p. 112°, but the production of $\beta\beta$ -diphenyl- $\alpha\alpha$ -dicyclohexylethylene glycol could not be certainly established. Catalytic hydrogenation of benzpinacol is accompanied by loss of OH in the initial stages, whereas benzpinacolin (PtO_2 in EtOH or Pr^iOH) gives $\alpha\alpha$ -diphenyl- $\alpha\beta$ -dicyclohexylethan- β -one (IV), m.p. 130°, which could not be hydrogenated further. (Perhydrogenation of $\text{CPh}_3\cdot\text{CO}_2\text{H}$ or CPh_4 appears impossible.) Ph cyclohexyl ketone is reduced by Zn dust and H_2SO_4 to diphenyldicyclohexylethylene glycol (V), two forms, m.p. 198° and 160°, respectively, isomerised by HCl in boiling AcOH to (IV). When similarly treated, dicyclohexyl ketone gives only dicyclohexylcarbinol, and pinacol formation is not achieved with Na-Hg, Mg-Hg, Al-Hg, or Mg activated by I. Reduction of CO of (IV) could not be effected by the usual reagents, whereas treatment with Mg cyclohexyl iodide in boiling PhMe is accompanied by the retropinacolin isomerisation and gives diphenyldicyclohexylethylene, m.p. 192°, degraded by O_3 to $\text{C}_6\text{H}_{11}\cdot\text{COPh}$ and oxidised by BzO_2H and then hydrated to (V). H. W.

Tricyclohexylmethane series. III. Tri-*p*-cyclohexylphenylcarbinol. Interaction of tri-cyclohexylmethyl bromide with metals. O. NEUNHOEFFER (Annalen, 1936, 526, 58—65).—Treatment of Me *p*-cyclohexylbenzoate with Mg *p*-cyclohexylphenyl iodide (I) in Et_2O affords *pp'*-dicyclohexyldiphenyl (II), m.p. 205°, *pp'*-dicyclohexylbenzophenone, m.p. 135°, and tri-*p*-cyclohexylphenylcarbinol (III), m.p. 168°. The constitution of (III) is assured by its production with (II) and *p*-cyclohexylbenzoic acid from (I) and CO_2 . (III) is not transformed into the corresponding halide by HCl in various media, PCl_3 , PCl_5 , SiCl_4 , SnCl_4 , SOCl_2 , AcCl , or AcBr or into the corresponding ether by HCl-MeOH, Me_2SO , and alkali, MeI and alkali or alkali metal, Me_2SO_3 and acid, $\text{CH}(\text{OEt})_3$ and various catalysts, or by CH_2N_2 in presence or absence of catalyst. cyclohexylbenzene, AlCl_3 , and CCl_4 do not appear to yield tri-*p*-cyclohexylphenylmethyl chloride.

Interaction of phenyldicyclohexylmethyl bromide with Ag in C_6H_6 is complicated by the elimination of HBr; this is avoided when Et_2O is used as solvent, in which case the reaction proceeds much more slowly. The final products are phenyldicyclohexylmethane and phenylcyclohexylcyclohexylidenemethane, which is quantitatively hydrogenated to tricyclohexylmethane. The initially formed radical is therefore almost completely disproportionated, and there is no evidence of its existence in appreciable amount at any stage of the change. A more complex product (IV) is also produced. Interaction of tricyclohexylmethyl bromide (V) with Ag gives similar results, except that (IV) is not formed. With Na-K (V) gives exclusively dicyclohexylcyclohexylidenemethane, m.p. 52°. The cyclohexyl residue does not appear, therefore, to facilitate radical formation. H. W.

Tricyclohexylmethane series. IV. Reaction-kinetic investigations with esters of secondary alcohols. O. NEUNHOEFFER and R. SCHLÜTER (Annalen, 1936, 526, 65—71).—The rates of hydrolysis

of several H succinates by alkali have been determined at various temp., the end-points being determined electrometrically or by means of phenolphthalein if a brisk stream of N_2 is passed over the surface of the liquid. The energy of activation and the action const. are calc. The high energy of activation of $\text{CHPr}_2\cdot\text{OH}$ and the low action const. of dicyclohexylcarbinol are remarkable; dicyclopentylcarbinol (II) is intermediate. With the first-named substance the slowness of the reaction is due to the necessity for the encounter of unusually activated mols. With (I) particularly activated mols. are unnecessary, but of the total contacts only a small proportion enter the sensitive zone and thus lead to reaction. It appears from a model that the Pr^i group can and must for reaction be forced to the side with a certain expenditure of energy, whereas this is not possible with the cyclohexyl residue. This shielding can be so complete that an expected action cannot occur, e.g., the hydrolysis of Et dicyclohexylacetate. The effect is sp. and not \propto the space demand of substituents. The following H succinates are described: benzhydryl, m.p. 78°; phenylcyclohexylcarbinyl, m.p. 110°; diisopropylcarbinyl, m.p. 61°; dicyclopentylcarbinyl, m.p. 80°; dicyclohexylcarbinyl, m.p. 132°; ditert-butylcarbinyl, m.p. 59°. Mg cyclopentyl chloride (III) in Et_2O is converted by CO_2 into cyclopentanecarboxylic acid, b.p. 110°/14 mm., with smaller amounts of cyclopentanol, dicyclopentyl, dicyclopentyl ketone, and dicyclopentylcarbinol. (III) and Et cyclopentanecarboxylate afford (II), b.p. 68°/0.2 mm., m.p. 47.5°. H. W.

Hydrogenation of acetylenic compounds. XXVI. Catalytic hydrogenation of α -glycols of the acetylene series. J. S. SALKIND and E. E. MARTINSON (J. Gen. Chem. Russ., 1936, 6, 1085—1088).— $\text{CH}:\text{CPh}$, MgEtBr , and benzoin in Et_2O (8 hr. at 40°, then 4 days at room temp.) yield $\alpha\beta$ -dihydroxy- $\alpha\beta\delta$ -triphenyl- Δ^y -butinene (I), m.p. 173—177°, converted by H_2 (Pd catalyst) successively into cis-, m.p. 121—122°, and trans- $\alpha\beta\delta$ -triphenyl- Δ^y -butene- $\alpha\beta$ -diol (II), m.p. 160—165°, and $\alpha\beta\delta$ -triphenylbutylene $\alpha\beta$ -glycol, m.p. 148°. (II) is hydrogenated slightly more slowly than (I). R. T.

Chemical activation of sterols. I. Nature of floridin activation of cholesterol. L. YODER (J. Biol. Chem., 1936, 116, 71—80).—The fuller's earth, floridin, which is capable of activating cholesterol (I) antirachitically, contains SO_3 . A possible step in the activation is the conversion of dicholesteryl ether into cholesterilene. The latter is antirachitically activated in CCl_4 by SO_3 or in AcOH by $\text{H}_2\text{SO}_4 + \text{Ac}_2\text{O}$, and in the latter case it was possible to prepare active Ba and Ca, m.p. 320—325°, salts of cholesterilenesulphonic acid. A similar Ca salt and sulphonic acid were prepared also from (I). J. N. A.

Differentiation of ergosterol from cholesterol. V. E. LEVINE and F. M. MCKAY (Proc. Soc. Exp. Biol. Med., 1936, 33, 546—549).—Irradiated and non-irradiated ergosterol (I) (< 0.01 mg. in 2 c.c. of CHCl_3) give a yellow or orange colour with 2 c.c. of a mixture of 2% aq. Na_2SeO_3 (3 vols.) and conc. HCl (1 vol.). 1 mg. of calciferol gives the same depth of colour as 0.2 mg. of (I) and cerevisterol gives a positive reaction,

but irradiated and non-irradiated cholesterol (II), carotene, and cholic acid give no colour. 0.025 mg. of (I) in presence of 100 mg. of (II) is detected by the test. W. McC.

Reaction between α -ketonic acids and α -amino-acids. R. M. HERBST (J. Amer. Chem. Soc., 1936, 58, 2239—2243).— α -NH₂-acids and α -CO₂H-acids are now considered (cf. A., 1935, 82) to react thus: $\text{COR}'\cdot\text{CO}_2\text{H} + \text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2\text{H}\cdot\text{CR}'\cdot\text{N}\cdot\text{CHR}\cdot\text{CO}_2\text{H} \rightarrow$

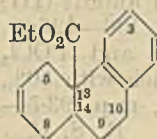
$\text{CO}_2 + \text{CHR}'\cdot\text{N}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ (I) or $\text{CHR}'\cdot\text{N}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ (II) (according to nature of R and R'; decarboxylation occurring at the same time as the tautomeric change); $(\text{I}) + \text{H}_2\text{O} \rightarrow$

$\text{R}'\text{CHO} + \text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H}$; $(\text{II}) + \text{H}_2\text{O} \rightarrow \text{RCHO} + \text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H}$. The compounds quoted in brackets are formed from AcCO_2H and the following: $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ [PhCHO, alanine (III)]; (III) [MeCHO; practically all (III) recoverable]; leucine [*isovaleraldehyde*, (III)]; α -amino- α -*p*-anisylacetic acid (IV) [*p*-OMe·C₆H₄·CHO, (III)]; *p*-methoxyphenylalanine [MeCHO, little (III), γ -hydroxy- α -keto- δ -*p*-anisylvalerolactone, m.p. 160° {phenylhydrazone, m.p. 163° (decomp.)}, which results from the condensation of *p*-OMe·C₆H₄·CH₂·CHO with AcCO_2H]; glutamic acid [(III)]; $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ [a little MeCHO; reaction is very slow (cf. *loc. cit.*)]; α -amino- α -phenylbutyric acid [COPhEt, MeCHO, little (III)]; cystine [MeCHO, resinous material]; *S*-ethylcysteine [MeCHO, (III), SEt·CH₂·CHO (*dimedon* derivative, m.p. 93—94°)]; *S*-phenylcysteine [MeCHO, (III), PhSH, Ph₂S₂, and (by continuous distillation) SPH·CH₂·CHO (*dimedon* derivative, m.p. 127—128°)]; *S*-benzylcysteine [MeCHO, (III), CH₂Ph·SH, and (as above) CH₂Ph·S·CH₂·CHO (*dimedon* derivative, m.p. 88—89°); 2:4-dinitrophenylhydrazones, m.p. 156—157°)]. CH₂Ph·CO·CO₂H and cystine give a little phenylalanine; aldehydes could not be found. COPh·CO₂H and (III) afford traces of CO₂ and PhCHO; similarly, (IV) gives PhCHO and *p*-OMe·C₆H₄·CHO, cystine yields NH₂·CHPh·CO₂H, and *S*-ethylcysteine furnishes SEt·CH₂·CHO. All m.p. are corr. H. B.

Synthesis of phenanthrene and hydrophenanthrene derivatives. V. Addition of dienes to cyclic $\alpha\beta$ -unsaturated esters. L. F. FISER and H. L. HOLMES (J. Amer. Chem. Soc., 1936, 58, 2319—2322).—Et 3:4-dihydro-1-naphthoate (I) and its 7-OMe-derivative add dienes slowly and incompletely, yielding the hexahydrophenanthrene esters, which are practically unaffected by 10% KOH and are thus readily freed from starting material. The new compounds are related structurally to morphine.

Et₂ α -oxalyl- γ -phenylbutyrate (from Et γ -phenylbutyrate, Et₂C₂O₄, and NaOEt) is hydrolysed (15% H₂SO₄) to α -keto- δ -phenylvaleric acid, m.p. 68—69.5°; the Et ester, b.p. 164°/13 mm., and 65% H₂SO₄ at 100° (bath) followed by 5% NaOH give 3:4-dihydro-1-naphthoic acid, m.p. 120—121°, dehydrogenated (S at 230—240°) to α -C₁₀H₇·CO₂H. Et γ -*p*-anisylbutyrate similarly leads to α -keto- δ -*p*-anisylvaleric acid, m.p. 65—74° (camphor-like) (Et ester, b.p. 190—192°/10 mm.), and 7-methoxy-3:4-dihydro-1-naphthoic acid, m.p. 116—117° [Et ester (II), b.p. 186—187°/9 mm.], which is reduced (Adams) to the 1:2:3:4-

tetrahydro-acid, m.p. 137.5—138.5°, and dehydrogenated (S at 230—240°) to 7:1-OMe·C₁₀H₆·CO₂H. The distillable product from (I) and (CH₂)₂·CH· after treatment with 10% KOH affords 21% of Et 5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylate (III), b.p. 164—166°/5 mm. [free acid, m.p. 141.5—142.5° (previous softening),



(III.)

obtained from (III) and EtOH·NaOEt at 170°, is dehydrogenated (Se at 300°) to phenanthrene]; (II) similarly yields 13% of the Et ester, b.p. 202—204°/14 mm., of 3-methoxy-5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylic acid, m.p. 139.5—141° (previous softening), whilst (I) and (CH₂)₂·CMe· give 27% of the Et ester, b.p. 166°/4 mm., m.p. 49.5—50°, of 6:7-dimethyl-5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylic acid, m.p. 168—169° (previous softening) (dehydrogenated to 2:3-dimethylphenanthrene). All m.p. are corr. H. B.

Action of thionyl chloride on esters of salicylic acid in presence of catalysts. J. A. KUNDARGI, Y. M. CHAKRADEO, and S. V. SHAH (Current Sci., 1936, 5, 198).—Small amounts of Zn and Fe dusts and chlorides of Zn, Fe, Sn, Bi, or Sb catalyse the formation of ester disulphides (73% yield) from alkyl salicylates and SOCl₂ (100% excess of SOCl₂, i.e., 1 mol. per mol. of ester). Reaction probably occurs by way of S₂Cl₂, since the same catalysts cause formation of the same products from S₂Cl₂ and *o*-OH·C₆H₄·CO₂H or its esters; the O from the SOCl₂ could not be located and may be used by oxidation of part of the ester. R. S. C.

Reaction between ethyl ketomalonate and aromatic hydrocarbons. I. Condensations in the presence of stannic chloride. T. ANDO (J. Chem. Soc. Japan, 1935, 56, 745—756).—With C₆H₆, Et phenyltartronate, hydrolysed to mandelic acid, is produced. *p*-Tolyl-, m.p. 36—39.2°; 2:3-dimethylphenyl-, b.p. 173—175°/7 mm., and 2:6-dimethylphenyl-, b.p. 177—180°/7 mm., -tartronic esters are obtained similarly and hydrolysed to 4-methyl-, m.p. 145—146°, 2:3-, m.p. 135—136°, and 2:6-dimethyl-, m.p. 177—178°, -mandelic acid, respectively. CH. ABS. (r)

Derivatives of *o*-xylene. S. MURAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 180—194).—*o*-C₆H₄(CH₂Br)₂ (I) and KCN in aq. EtOH gave in one experiment *o*-C₆H₄(CH₂CN)₂ and in another mainly *o*-ethoxymethylbenzyl alcohol (impure), b.p. 122—124°/17 mm., oxidised by Na-Et₂O in air to *o*-OEt·CH₂·C₆H₄·CO₂H, m.p. 85—86°; CH₂Ph·OH and Na-Et₂O in air give BzOH. *o*-C₆H₄(CH₂·OMe)₂ [from (I) and NaOMe], b.p. 109—111°/16 mm., AcCl, and ZnCl₂ in CCl₄ give *o*-methoxymethylbenzyl chloride (not obtained pure), converted by KCN into *o*-methoxymethylphenylacetone nitrile, b.p. 151—153°/17 mm., which with KOH-EtOH gives *o*-methoxymethylphenylacetic acid (II), m.p. 52—54°; with HBr at 150° gives *o*-hydroxymethylphenylacetic lactone (III), m.p. 82.5—83.5° [also obtained by H₂SO₄ (1:2)], or at lower temp. also some *o*-bromomethylphenylacetone nitrile, m.p. 92—92.5°; with conc. HCl gives *o*-chloromethylphenylacetic acid (IV), m.p. 118—

118.5°, and with $\text{NH}_3\text{-EtOH}$ affords the *amide*, m.p. 117—118°, of (II) and a *substance*, m.p. 209—211° (III) and HCl-EtOH give the *Et* ester, b.p. 162.5—163.5°/21 mm., of (IV), which with aq. alkali yields (III) (10%) and a polymerised *substance*, m.p. 124—124.5°. (II) and SOCl_2 give an oil (16.8% Cl), b.p. 126—136°/4 mm., which with 2*N*-KOH affords (III) and *substances*, $\text{C}_{18}\text{H}_{14}\text{O}_2(\text{OMe})_2$, m.p. 126—126.3°, and $\text{C}_{28}\text{H}_{36}\text{O}_6$, m.p. 198—199°. (II) and POCl_3 give two oils, the higher-boiling of which with 50% KOH affords *o*-benzylphenylacetic acid, m.p. 93.5—94.5°. R. S. C.

Deuterium as an indicator in stereochemical investigations. H. ERLÉNMEYER, H. SCHENKEL, and A. EPPRECHT (*Nature*, 1936, 138, 547, and *Helv. Chim. Acta*, 1936, 19, 1053—1056).—When recryst. from D_2O at 60°, mandelic acid (I) retains its optical activity and 2 H are exchanged. When heated at 140° for 51 hr. in D_2O , the acid isolated is optically inactive, and 2 H are again exchanged for 2 D. Heating (I) in a solution of NaOD for 16 hr. at 100° gives a fully racemised acid. The results support the Werner-Hund and not the enolisation conception of racemisation. The change in optical activity which *l*-(I) undergoes on reacting with D_2O at 60° is reported. L. S. T.

Kinetics of benzilic acid rearrangement.—See A., I, 35.

Reactions of ethyl cyclohexanone-2-carboxylate and ethyl cyclopentanone-2-carboxylate with unsaturated methyl ketones. W. S. RAPSON (*J.C.S.*, 1936, 1626—1628).—Ethylideneacetone with *Et* cyclohexanone-2-carboxylate (I) and KOEt-EtOH yields *Et* 2-*keto*-4-methyl- $\Delta^{1:9}$ -octalin-10-carboxylate, m.p. 76°, b.p. 165—170°/1 mm. Similarly (I) with styryl Me ketone (II) yields *Et* 2-*keto*-4-phenyl- $\Delta^{1:9}$ -octalin-10-carboxylate, m.p. 150°, b.p. 215—220°/1 mm., and with anisylideneacetone (III) the corresponding 4-*p*-anisyl compound, m.p. 112—113°, b.p. 235—240°/6 mm. Neither product was hydrolysed by conc. alkali or by conc. HCl on long boiling, nor could any ketonic derivatives be prepared. *Et* cyclopentanone-2-carboxylate (IV), however, with (II) and KOEt-EtOH gives η -*keto*- δ -carbethoxy- ϵ -phenyl-nonoic acid (V), which exists in two forms, m.p. 126.5—127.5° and m.p. 110—111° (*Me* ester, m.p. 103—104°), hydrolysed to the δ -carboxylic acid, α -(γ' -*keto*- α' -phenyl-*n*-butyl)adipic acid, which exists in two stereoisomeric racemic forms, m.p. 173—174°, and m.p. 231—232° with evolution of gas. When the condensation was carried out in C_6H_6 instead of EtOH there was also formed some *Et* 1-(α -phenyl- γ -*keto*-*n*-butyl)cyclopentan-2-onecarboxylate, m.p. 88—89.5°, converted into (V), m.p. 110—111°, by NaOH-EtOH . (III) and (IV) with KOEt-EtOH give η -*keto*- δ -carbethoxy- ϵ -*p*-methoxyphenyl-nonoic acid, m.p. 121—122°. H. G. M.

Syntheses in the naphthalene group. I. Syntheses of 4-hydroxy-1-arylnaphthalene-2-carboxylic acids, 4-hydroxy-1-arylnaphthalenes, and of 2-hydroxy-3:4-benzofluorenones. W. BORSCHE [with S. KETTNER, M. GILLIES, H. KÜHN, and R. MANTEUFFEL] (*Annalen*, 1936, 526, 1—22).—

Gradual addition of AlCl_3 to $\gamma\gamma$ -diphenylitaconic anhydride in PhNO_2 at room temp. gives 1-phenylindonyl-2-acetic acid (I), m.p. 166—167° (2:4-dinitrophenylhydrazones, m.p. 265°).

$\text{CPh}_2\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and NaOAc in boiling Ac_2O yield *Et* 4-acetoxy-1-phenylnaphthalene-2-carboxylate, m.p. 87—88°, hydrolysed by boiling 10% NaOH to 4-hydroxy-1-phenylnaphthalene-2-carboxylic acid (II), m.p. 212—214° [*Me* ester (III), m.p. 174—175°; *Ac* derivative, m.p. 200—202°], converted by Br in AcOH into 3-bromo-4-hydroxy-1-phenylnaphthalene-2-carboxylic acid, m.p. about 230° (decomp.). (II) is decarboxylated by Cu powder in boiling quinoline to 1-phenyl-4-naphthol (IV), m.p. 140°. (III), CH_2O , and conc. HCl in AcOH at 110° afford the lactone, $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\text{C}(\text{CH}_3)\text{C}(\text{CO})\text{CPh}\rangle\text{O}$, m.p. 266°, of 4-hydroxy-1-phenyl-3-hydroxymethylnaphthalene-2-carboxylic acid. Reduction of (II) by Na and AcOH in MeOH at 50° gives the lactone, m.p. 156°, of 4-hydroxy-1-phenyl-1:4-dihydronaphthalene-2-carboxylic acid (*Na* salt). 9-*Keto*-2-acetoxy-3:4-benzofluorene, m.p. 177° after softening (2:4-dinitrophenylhydrazones, m.p. about 290°), obtained from (I) and boiling Ac_2O containing NaOAc , is hydrolysed by *N*- NaOH to 9-*keto*-2-hydroxy-3:4-benzofluorene (V), m.p. 258°, also obtained slowly from (II) and ice-cold, conc. H_2SO_4 . Analogous ring closures from γ -phenyl- γ -*p*-anisylitaconic acid lead to methoxyphenylindonylacetic acid, m.p. 147—149° (2:4-dinitrophenylhydrazones, decomp. about 250°), non-cryst. 4-acetoxy- γ -methoxy-1-phenylnaphthalenecarboxylic acid, 4-hydroxy-7-methoxy-1-phenylnaphthalenecarboxylic acid, m.p. 190—192°, and 9-*keto*-2-hydroxy- γ -methoxy-3:4-benzofluorene, m.p. 255—258° (*Ac* derivative, m.p. 209—210°). Addition of piperonylnitrile in C_6H_6 to MgPhBr in Et_2O yields benzopiperone, b.p. 205—210°/16 mm., m.p. 55° (*oxime*, m.p. 138—139°; 2:4-dinitrophenylhydrazones, m.p. 220°), which condenses with $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ to the *b*-*Et*₁ ester, m.p. 148°, of γ -phenyl- γ -3:4-methylenedioxyphenylitaconic acid, whence 4-hydroxy-6:7-methylenedioxy-1-phenylnaphthalene-2-carboxylic acid, m.p. 254°.

$\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ is transformed by NaI in COMe_2 in the dark into *Et*₂ iodosuccinate, b.p. 141—144°/18 mm., which is converted by Zn filings and COPh_2 in boiling C_6H_6 into *Et* $\gamma\gamma$ -diphenylparaconate, m.p. 152°. The latter substance is stable towards heat. It is hydrolysed by 1 or 2 mols. of KOH to the *b*-*Et*₁ ester, m.p. 136°, of γ -hydroxy- $\gamma\gamma$ -diphenylpyruvic acid with varying amounts of COPh_2 and $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, by a large excess of KOH also to di-phenylitaconic acid, m.p. 172°, and by conc. HCl to $\gamma\gamma$ -diphenylisocrotonic acid, m.p. 114—115°. Cyclisation of it with conc. H_2SO_4 at 0° leads to (I) and phenylhydrindoneacetolactone, whereas treatment with PCl_3 affords (V). *Et* γ -phenyl- γ -3:4-methylenedioxyphenylparaconate has m.p. 161°.

COPh_2 , $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, Mg turnings, and Zn filings in boiling C_6H_6 yield benzpinacone, m.p. 184—185°. $(\text{CH}_2\cdot\text{COCl})_2$ and C_6H_6 in presence of AlCl_3 give γ -hydroxy- $\gamma\gamma$ -diphenylbutyric acid, m.p. 135° (decomp.) (*Me* ester, m.p. 91°); the corresponding lactone, m.p. 92—93°, is converted by distillation/760 mm. or by PCl_3 into (IV).

CHPh_2CHO and $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ at 100° give $\gamma\gamma$ -diphenyl- Δ^8 -butenoic acid, m.p. $114-115^\circ$; the *Et* ester, b.p. $165-170^\circ/0.1$ mm., is converted by Br in AcOH into β -bromo- $\gamma\gamma$ -diphenylbutyrolactone, m.p. 132° , transformed by boiling $\text{C}_5\text{H}_5\text{N}$ into $\gamma\gamma$ -diphenylcrotonolactone, m.p. 130° . The acid is transformed by boiling PCl_3 or by NaOAc and Ac_2O followed by hydrolysis into (IV). PhOMe, $(\text{CH}_2\text{COCl})_2$, and AlCl_3 in CS_2 give 4:4'-dimethoxydiphenacyl, m.p. $108-109^\circ$ [*di*-2:4-dinitrophenylhydrazones, m.p. $197-198^\circ$ (decomp.)], β -anisoylpropionic acid (*Me* ester, identified by conversion into the 2:4-dinitrophenylhydrazones), and $\gamma\gamma$ -di-*p*-anisyl- Δ^8 -butenoic acid, m.p. $94-95^\circ$ (*Me* ester, m.p. 70°). The last-named acid is converted by boiling PCl_3 into 4-hydroxy-6-methoxy-1-*p*-anisyl-naphthalene, m.p. $165-166^\circ$. $(\text{CH}_2\text{COCl})_2$, veratrole, and AlCl_3 in CS_2 yield, after esterification, *Me* γ -veratroylpropionate, m.p. $90-91^\circ$, and *Me* $\gamma\gamma$ -diveratryl- Δ^8 -butenoate, b.p. $254-256^\circ/1$ mm., whence $\gamma\gamma$ -diveratryl- Δ^8 -butenoic acid, m.p. $128-129^\circ$. (IV) gives a *Bz* derivative, m.p. $73-74^\circ$, and 4-hydroxy-3-benzeneazo-1-phenyl-naphthalene, m.p. 165° H. W.

Spiro-compounds. I. New route to spiro-compounds. Synthesis of cyclohexanespirocyclopentane. N. N. CHATTERJEE (J. Indian Chem. Soc., 1936, 13, 536-541).—cycloHexanonecyanohydrin with $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$, Na, and EtOH, followed by $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, yields *Et*₂ α -cyano- α -(1-cyanocyclohexyl)glutarate, b.p. $220-225^\circ/8$ mm., which, stable to conc. HCl, is hydrolysed by 70% H_2SO_4 to the anhydride (*Et* ester, m.p. 46°) of α -1-carboxycyclohexylglutaric acid, m.p. 165° . The *Et*₃ ester, b.p. $164^\circ/4$ mm., of this condenses (Na in C_6H_6) to *Et*₂ cyclohexanespirocyclopentan-2-one-3:5-dicarboxylate, b.p. $174^\circ/4$ mm., which in boiling dil. H_2SO_4 slowly gives cyclohexanespirocyclopentan-2-one-5-carboxylic acid (I), m.p. 102° [*Et* ester, b.p. $132^\circ/5$ mm. (semicarbazone, m.p. 201°)]. (I) is reduced (Zn-Hg in HCl) to cyclohexanespirocyclopentan-5-carboxylic acid (II), of which the *Ca* salt yields cyclohexanespirocyclopentane. (I) is oxidised (HNO_3) to cyclohexane-1:1-dicarboxylic acid; (II) when dehydrogenated (Se) yields a small quantity of naphthalene.

E. W. W.

Retene. VII. Fluorenones and phenanthridones from retenediphenic acid. D. E. ADLSON and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 2236-2239; cf. A., 1936, 984).—Retenediphenic [3-methyl-4'-isopropylidiphenic] acid (I) and 95% H_2SO_4 at room temp. for 24 hr. give 1-methyl-7-isopropylfluorenone-5-carboxylic acid (II), m.p. $200.5-201^\circ$ [oxime, m.p. $249-250^\circ$ (decomp.); *Me* ester (III), m.p. $104-104.5^\circ$ (oxime, m.p. $151.5-152^\circ$)], whilst at $110-115^\circ/20$ min. dehydration occurs in the second possible manner and affords 6-methyl-2-isopropylfluorenone-5-carboxylic acid (IV), m.p. $156-156.5^\circ$ [oxime, m.p. $268-269^\circ$ (darkens $>250^\circ$); *Me* ester, m.p. $86.5-87.5^\circ$ (oxime, m.p. $173-174^\circ$)], together with some (II) and a little of a neutral compound, m.p. $194-195^\circ$. An inseparable mixture of products is formed at 60° , whilst at $175^\circ/2$ min. sulphonation occurs. The 2'-*Me* 2-H ester (V) of (I) with 95% H_2SO_4 at room temp. gives (III); at

110° , (II), (III), and (IV) are produced. (V) and conc. aq. NH_3 afford the 2'-monoamide, converted by KOBr in aq. KOH into 8-methyl-2-isopropylphenanthridone, m.p. $230-231^\circ$, which is oxidised (alkaline KMnO_4) to hemimellitic acid and differs from the (1-methyl-(7-)isopropylphenanthridone previously obtained (A., 1934, 646) by the Beckmann rearrangement of 1-methyl-7-isopropylfluorenoneoxime. Dry distillation of the anhydride of (I) gives 90% of 1-methyl-7-isopropylfluorenone (retene ketone), m.p. $89-90^\circ$, which could not be obtained by decarboxylation of (IV). All m.p. are corr. H. B.

Amino-acids. IX. Condensation of resorcyaldehyde with hippuric acid; 2:4-dihydroxyphenylalanine. V. DEULOFEU (Ber., 1936, 69, [B], 2456-2459; cf. A., 1935, 850).—Resorcyaldehyde, hippuric acid, NaOAc, and Ac_2O at $115-120^\circ$ give 3-benzamidoumbelliferone acetate (I), m.p. 190° , and the yellow azlactone, $\text{C}_{20}\text{H}_{15}\text{O}_6\text{N}$, m.p. $139-140^\circ$. Alkaline or acid hydrolysis of (I) or acid hydrolysis of the crude product of the above reaction affords 3-benzamidoumbelliferone, m.p. $284-285^\circ$ after softening, converted by boiling 8% NaOH into α -benzamido- β -2:4-dihydroxyphenylacrylic acid (III), m.p. 242° , also obtained similarly from (II). (III), NaOAc, and Ac_2O at 130° give (II). 2:4- $\text{C}_6\text{H}_3(\text{OMe})_2\text{CHO}$, hydantoin, NaOAc, and Ac_2O at $125-130^\circ$ yield 2:4-dimethoxybenzylidenehydantoin, m.p. 233° , reduced (Na-Hg in alkaline solution) to 2:4-dimethoxybenzylhydantoin (IV), m.p. 166° . (IV) is converted by boiling aq. $\text{Ba}(\text{OH})_2$ into 2:4-dimethoxyphenylalanine, m.p. 241° , demethylated [red P-HI (*d* 1.7)- Ac_2O] to 2:4-dihydroxyphenylalanine, m.p. $223-224^\circ$. Bisdibenzylidenediketopiperazine is reduced by Zn dust in boiling AcOH to *di*-2:4-dimethoxybenzoyldiketopiperazine, m.p. 209° . 2':4'-Dimethoxybenzylidene-2-thiohydantoin has m.p. 228° . H. W.

Choleic acids. VI. Isomerism and co-ordination valency; coloured choleic acids. W. MARX and H. SOBOTKA (J. Org. Chem., 1936, 1, 275-279; cf. A., 1932, 930, 944).—Deoxycholic acid gives choleic acids with the following, the co-ordination no. being stated in parentheses: oleic (8), m.p. 188° , elaidic (8), m.p. $187-188^\circ$, erucic (8), m.p. $193.5-194.5^\circ$, and brassidic acid (8), m.p. $193-194^\circ$, phenanthrene (3), m.p. $186-187^\circ$, anthracene (4), m.p. 193° , dibenzoyl- (3), m.p. $199.5-200.5^\circ$, and dicinnamoyl-methane (6), m.p. $195-196^\circ$, cinnamoyl (prep. by Ryan and Dunlea's method) (4), m.p. $190.5-191.5^\circ$, and dicinnamoyl-acetone (6), m.p. 191.5° . The solid diketone-choleic acids are more highly coloured than the solid diketones, but colorimetric investigation confirms the complete dissociation in solution indicated by other methods. The unsaturated acids are recovered from their choleic acids without isomerisation. R. S. C.

Glucosides of bile acids. I. E. DANE and T. BRADY (Z. physiol. Chem., 1936, 244, 241-244; cf. Lettré *et al.*, A., 1936, 1376).—The *Me* ester, m.p. $95-97^\circ$, of deoxycholic acid (I) in C_6H_6 with acetobromoglucose and AgOAc gives the acetate of the *Me* ester, m.p. $125-127^\circ$ or (from moist COMe_2) $135-136^\circ$, of the monoglucoside, m.p. $215-217^\circ$,

of (I). Very probably (I) unites with the glucose residue at the OH at C₍₃₎. W. McC.

Constitution of ursodeoxycholic acid. T. IWASAKI (Z. physiol. Chem., 1936, 244, 181—193; cf. Shoda, A., 1928, 666; Kaziro, A., 1931, 957).—The dehydro-derivative (I), m.p. 154°, of ursodeoxycholic acid (II), m.p. 203°, [α]_D²⁰ +57.07° (disformate, m.p. 170°; Me ester, m.p. 161°), with Zn-Hg in AcOH + HCl gives cholanic acid, also obtained from *ursocholadienic acid* (III), m.p. 150°, [α]_D²⁰ -43.75° in CHCl₃ (and chenocholadienic acid), by reduction with PtO₂-H₂. Partial reduction of (I) in EtOH with PtO₂-H₂ gives 3-hydroxy-7-ketocholanic acid (IV), m.p. 203°, [α]_D²⁰ -27.35° (acetate, m.p. 142°), also obtained from (II) by partial oxidation with CrO₃ in AcOH. In the same ways the dehydro-derivative (V) of chenodeoxycholic acid (VI) and (VI) yield (IV). (IV) distilled in a vac. at 340° gives 7-keto-3-cholanic acid, m.p. 149—150°, [α]_D²⁰ -74.82°, which, in EtOH, with PtO₂-H₂ yields 7-ketocholanic acid (VII) (Me ester, m.p. 78°; oxime, m.p. 240°), also obtained from (I) in AcOH by partial reduction with Zn-Hg + HCl. (VII) in EtOH + AcOH with PtO₂-H₂ gives 7-hydroxycholanic acid, m.p. 96—102° (+1H₂O, m.p. 95—98°), which yields thilobilianic acid with HNO₃. The semicarbazone of (II) with NaOEt at 180—185° gives lithocholic acid. (II) with KOBr gives a hydroxytricarboxylic acid, m.p. 242° (acetate, m.p. 253°), which with CrO₃ gives ursodeoxybilianic acid, m.p. 231°. (I) in EtOH with PtO₂-H₂ gives (VI), m.p. 140°, [α]_D²⁰ +12.5° in EtOH (Ba salt), the separation of which from bear's bile is described. (VI) with CrO₃ in AcOH yields (V), m.p. 153—154°, [α]_D²⁰ -26.85° in EtOH. (III) is obtained from (II) by heating at 320—346°/5 mm. The results show that (II) and (VI) differ only in the spatial positions of their OH groups, and that (II) is 3- α -7- β -dihydroxycholanic acid. W. McC.

Constitution of trihydroxybufosterocholanic acid and systematic degradation of cholic acid. V. T. SUMIZU and T. KAZUNO (Z. physiol. Chem., 1936, 244, 167—172; cf. A., 1934, 1219).—1 g. of Me trihydroxybufosterocholenate in AcOH yields with O₃ 0.05 g. of trihydroxybisorcholic acid (I), C₂₂H₃₆O₅, m.p. 283°, [α]_D²⁰ +9.74° in AcOH. Me cholate with MgMeI gives the corresponding carbinol, m.p. 177—177.5° [tetra-acetate (II), m.p. 111.5—112°]. (II) with CrO₃ in AcOH gives the triacetate, m.p. 106—108°, of *norcholic acid*, C₂₃H₃₈O₅ + H₂O and +0.5H₂O, m.p. 183.5°, [α]_D²⁰ +38.37° in MeOH [Ba salt; Me ester (III), m.p. 155°; Et ester, m.p. 144—145°], which with CrO₃ in AcOH gives dehydronorcholic acid, m.p. 303—306°. (III) with MgMeI gives the corresponding carbinol, m.p. 236° [tetra-acetate, m.p. 138°, which with CrO₃ in AcOH followed by hydrolysis gives (I) (Et ester, m.p. 149°)]. W. McC.

Bile acids of alligator tortoises. K. YAMASAKI and M. YUUKI (Z. physiol. Chem., 1936, 244, 173—180).—The residue left after CHCl₃ extraction of the bile of the tortoise *Amyda japonica* yields on alkaline hydrolysis taurine and a lactone (I), C₂₇H₄₄O₅ or C₂₈H₄₆O₅, m.p. 208°, [α]_D²⁰ +32.87° in EtOH, of trihydroxysterchocholic acid. (I) with warm dil. aq. NaOH gives an acid, m.p. 140° (Me ester, m.p.

150—155°), reconverted into (I) by heating at about 140°. (I) with CrO₃ in AcOH gives equal amounts of a triketolactone (II), C₂₇H₃₈O₅ or C₂₈H₄₀O₅, m.p. 304—306° (decomp.) (oxime, decomp. 250—260°), and a tetraketo-acid (III), m.p. 214°, [α]_D²⁰ -21.62° [Me ester (IV), m.p. 131—133°; oxime of (IV), m.p. 200—202°]. (II) with CrO₃ in AcOH gives a tetraketo-acid, m.p. 205°, also obtained by boiling (III) with HCl. The CHCl₃ extract yields the lactone (V), m.p. 228°, [α]_D²⁰ +34.5° in EtOH, of tetrahydroxysterchocholic acid, C₂₉H₅₀O₂ or C₂₈H₄₈O₂. (V) with CrO₃ in AcOH yields the corresponding tetraketone, m.p. 155—156° (tetraoxime, m.p. 160°). W. McC.

Bile acids. LVI. Dihydroxycholenic acids. H. WIELAND, E. DIETZ, and H. OTTAWA (Z. physiol. Chem., 1936, 244, 194—202; cf. A., 1936, 983; Yamasaki, A., 1933, 1162; Callow, A., 1936, 841).—The diacetate (I), m.p. 136—137°, of Me apocholate combines with BzO₂H and the product yields 3:12-dihydroxycholadienic acid, m.p. 237—240°, when boiled for 30—60 min. with 0.5N-KOH in EtOH. When the temp. is 80° and the concn. of alkali 0.3N a tetrahydroxy-acid, m.p. 197—198°, is obtained. (I) treated with O₃ followed by reduction with Pd-H₂ gives an acid substance (an ester) and a neutral substance. Dihydroxycholenic acid in AcOH shaken with conc. HCl gives isodihydroxycholenic acid (II), also obtained from β -apocholic acid and conc. HCl. (II) with BzO₂H in CHCl₃ gives the oxide, m.p. 182—184°, and with Br in MeOH gives an acid [compound (III) with EtOAc, m.p. 162—163°]. (III) with PtO₂-H₂ gives an acid, m.p. 220—230°, and with mineral acids a deep violet colour. W. McC.

Bile acids. LV. Nitrogenous product obtained from bilianic acid by oxidation with nitric acid. Production of cilianic acid by two methods. M. SCHENCK (Z. physiol. Chem., 1936, 244, 345—252; cf. A., 1936, 1109).—One CO₂H of the acid (I) C₂₄H₃₅O₁₀N is present as CO·NH₂. (I) gives with HNO₃ at 100° biloidanic acid in poor yield, with alkaline aq. KMnO₄ cilianic acid (II), and with Zn and aq. NH₃ a tribasic acid, C₂₄H₃₅O₅N, decomp. 222°, which with alkaline KMnO₄ gives (II). W. McC.

Synthesis of phenanthrene and hydrophenanthrene derivatives. IV. Hydroxylated compounds. L. F. FIESER and E. B. HERSHBURG (J. Amer. Chem. Soc., 1936, 58, 2314—2318).—Hydroxyphenanthrene-1:2-dicarboxylic and octahydrophenanthrene-11:12-dicarboxylic anhydrides are prepared by methods similar to those previously described (A., 1935, 1495; 1936, 203). PhOMe (0.4 mol.) and (-CH₂·CO)₂O (0.42 mol.) in C₂H₂Cl₄ + PhNO₂ with AlCl₃ (0.84 mol.) at 0—5° give 85% of β -*p*-anisoylpropionic acid; β -veratroyl- (67%) and β -4-methoxy-1-naphthoyl-propionic acid (98%) are similarly obtained from *o*-C₆H₄(OMe)₂ and 1-C₁₀H₇·OMe (in C₂H₂Cl₄ alone), respectively. The above acids are reduced (modified Clemmensen; cf. Martin, A., 1936, 1249) to γ -*p*-anisyl- [Et ester (I), b.p. 177—178°/15.5 mm.], γ -3:4-dimethoxyphenyl- [Et ester (II), b.p. 186—189°/8.5 mm.], and γ -4-methoxy-1-naphthylbutyric acid, m.p. 129—130° [Et ester (III), b.p. 239—242°/16 mm.], respectively.

Condensation (KOEt) of (I), (II), Et γ -3-methoxy-4-methylphenyl- and γ -*m*-anisyl-butyrate, and (III) with $\text{Et}_2\text{C}_2\text{O}_4$ and subsequent treatment of the oxalyl derivatives with 60–84% H_2SO_4 gives 7-methoxy- (IV), m.p. 164.5–165°, 6:7-dimethoxy- (V), m.p. 192.5–193°, 6-methoxy-7-methyl- (VI), m.p. 189.8–190.3°, and 6-methoxy-, m.p. 164–165°, 3:4-dihydronaphthalene-1:2-dicarboxylic anhydride and 9-methoxy-3:4-dihydronaphthalene-1:2-dicarboxylic anhydride, m.p. 194–197°, respectively. The following were formed as by-products and also by dehydrogenation (S at 240–250°) of the 3:4- H_2 -derivatives: 6-methoxy-, m.p. 210–210.5°, 7-methoxy-, m.p. 194–195°, and 6-methoxy-7-methyl-, m.p. 215–215.5°, -naphthalene- and 9-methoxyphenanthrene-1:2-dicarboxylic anhydride*, m.p. 251–252°. (IV), (V), and (VI) with butadiene in dioxan at 160–180° afford 75–85% of 6-methoxy-, m.p. 126.5–127°, 6:7-dimethoxy-, m.p. 138.6–138.8°, and 7-methoxy-6-methyl- (VII), m.p. 152–152.5°, -1:4:9:10:11:12-hexahydrophenanthrene-11:12-dicarboxylic anhydride, respectively, reduced (H_2 , PtO_2 , AcOH) to the -1:2:3:4:9:10:11:12-octahydro-derivatives, m.p. 159–159.5°, 146.5–147°, and 149.5–150°, respectively, which are demethylated (48% HBr , AcOH) to 6-hydroxy-, m.p. 160–160.5°, 6:7-dihydroxy- (VIII), m.p. 147.5–148.5° (Ac_2 , m.p. 151.5–152°, and Bz_2 , m.p. 175–175.5°, derivatives), and 7-hydroxy-6-methyl-, m.p. 134.5–135.5°, -1:2:3:4:9:10:11:12-octahydrophenanthrene-11:12-dicarboxylic anhydride, respectively. 6-Methoxy-2:3-dimethyl-1:4:11:12:13:14-hexahydrochrysene-13:14-dicarboxylic anhydride, m.p. 181–182°, is prepared from the appropriate anhydride and $(\text{CH}_2\text{CMe})_2$ at 100°. Me_2 6:7-dimethoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene-11:12-dicarboxylate has m.p. 134.5–135.5°. The K_2 salt from (VII) heated at 350–420° gives a product which is dehydrogenated (Se at 300°) to 2-methoxy-3-methylphenanthrene, m.p. 132–132.5° (picrate, m.p. 142.5–143°). All m.p. are corr.

Compounds marked * are oestrogenic (method: Pincus and Werthessen, A., 1936, 1148); (VIII) is the most active, and is more potent than ketotetrahydrophenanthrene. Contrary to the previous statement (A., 1935, 1495), phenanthrene-1:2-dicarboxylic anhydride and its 3:4- H_2 -derivative are inactive.

H. B.

Transformations of phthalylmalonic ester. J. SUSZKO and L. WÓRCIŃSKI (Ber., 1936, 69, [B], 2452–2455).— Et_2 phthalylmalonate (I) is not appreciably affected by conc. H_2SO_4 at 12–15°, whereas at 80° 1:3-diketohydrindene (II), bindone (III), and truxenequinone (IV) are produced. The formation of the latter substances can be suppressed by working at a somewhat lower temp., but phthalylacetic acid (V) is then formed in proportion which increases with fall of temp. (II), (III), and (IV) are also formed from (V) and conc. H_2SO_4 at 80°, but at lower temp. (V) is mainly unchanged, and hence cannot be regarded as an intermediate in the transformation of (I) into (II), (III), and (IV). (I) and boiling 75% H_2SO_4 give very little (II) and mainly (V) accompanied by *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and *o*-

$\text{C}_6\text{H}_4\text{Ac}\cdot\text{CO}_2\text{H}$; under suitable conditions satisfactory yields of the last-named compound are obtained. With 50% H_2SO_4 (V) does not appear to be formed, the products being unchanged (I), *o*- $\text{C}_6\text{H}_4\text{Ac}\cdot\text{CO}_2\text{H}$, and *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$, the last in varying and non-reproducible yield.

H. W.

Constituents of hinokiol. VI. S. KEIMATSU, T. ISHIGURO, and Y. NAKAMURA (J. Pharm. Soc. Japan, 1935, 55, 775–780).—Reduction ($\text{Pd}\cdot\text{C}$ or $\text{Na}\cdot\text{Hg}$) of $\alpha\alpha'$ -dipiperonylidene succinic acid yields *cis*-, decomp. 236–238° [anhydride (I), m.p. 160–161°], and *trans*-, decomp. 191–193°, - $\alpha\alpha'$ -dipiperonyl-succinic acids. (I) with $\text{Al}\cdot\text{Hg}$ affords $\alpha\beta$ -dipiperonyl-butyrolactone, m.p. 106–107°. CH. ABS. (r)

Action of alkalis on mixtures of aromatic aldehydes. J. C. BAILAR, jun., A. J. BARNEY, and R. F. MILLER (J. Amer. Chem. Soc., 1936, 58, 2110–2111).—When a mixture of PhCHO (5 g.) and *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (I) (5 g.) is treated with 50% KOH (20 g.), the PhCHO undergoes the Cannizzaro reaction, but (I) is unaffected. With $\text{PhCHO} + m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and 14% KOH the former is unaffected, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ and *m*- and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHO}$ in admixture with PhCHO or *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (and in one case piperonal) are preferentially oxidised to the $\text{C}_6\text{H}_4\text{Hal}\cdot\text{CO}_2\text{H}$ at the expense of the second aldehyde; crossed Cannizzaro reactions can therefore take place.

H. B.

Condensation of aromatic aldehydes and amines in mineral acid solution. R. GARZULY-JANKE (Magyar chem. Fol., 1935, 41, 4–8; Chem. Zentr., 1936, i, 324–325).—The following condensation products (1 mol. of each ingredient) are described [(I) = salicylaldehyde; (II) = PhCHO ; (III) = arsanilic acid]: (I)- $\text{NH}_2\text{Ph} + \text{HCl}$, m.p. 94°; + HBr , m.p. 114°; + HNO_3 , m.p. 125°; + H_2PtCl_6 ; + HClO_4 , m.p. 140–141°; (I)-*o*-toluidine, HCl , m.p. 73–74°; (I)-*m*-toluidine, HBr , m.p. 197–198°; (I)-*o*-nitroaniline + HCl , m.p. 171°, and HBr , m.p. 185°; (I)-*m*-nitroaniline, HCl , m.p. 173°; (I)-*p*-nitroaniline, HNO_3 , m.p. 96°; (I)-*p*-aminophenol- HCl , m.p. 157°; (II)-*m*-nitroaniline + HCl , m.p. 177°, and + HNO_3 , m.p. 180°; (II)- $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2\cdot\text{HCl}$, m.p. 162–163°; (II)-*p*-nitroaniline, HCl , m.p. 188°; (I)-(III), HCl , (I)-(III), HNO_3 ; *p*-hydroxybenzaldehyde-(III), HCl ; *p*-methoxybenzaldehyde-(III), HNO_3 ; resorcyaldehyde-(III) + HCl and + HNO_3 ; protocatechualdehyde-(III) + HCl and + HNO_3 ; piperonal-(III) + HCl and + HNO_3 .

H. N. R.

Solubility in alkalis of some phenolic derivatives. G. IGLESIAS (Anal. Fis. Quím., 1935, 33, 119–125).—Contrary to Torrey *et al.* (A., 1913, i, 649) 2:1- $\text{C}_{10}\text{H}_6\text{Ac}\cdot\text{OH}$ (I) and its derivatives are much less sol. in alkali than 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHO}$ (II) and its derivatives. (I) is sol. in 20% Na_2CO_3 but (II) is dissolved only by 10% NaOH ; the $\text{NHPh}\cdot\text{N}$, NPh , and $\text{N}\cdot\text{C}_{10}\text{H}_7$ derivatives of (I) are sol. in 10% NaOH , but those of (II) are dissolved only by 50% KOH . 2-Acetyl- α -naphthol anil, m.p. 121°, and 2-acetyl-1-naphthyl acetate semicarbazone, m.p. 215°, are described.

F. R. G.

Synthesis of γ -resorcyaldehyde. R. C. SHAH and M. C. LAIWALLA (Current Sci., 1936, 5, 197—

198).—Me β -resorcyate affords (Gattermann; AlCl_3 -dry Et_2O) Me 2:4-dihydroxy-3-aldehydobenzoate and thence (hydrolysis and H_2O at 100–110°) a 30% yield of γ -resorcyaldehyde or (Clemmensen and methylation) Me 2-hydroxy-6-methoxy-*m*-toluate.

R. S. C.

Stereoisomerism of alicyclic oximes. II. W. HÜCKEL and W. DOLL (Annalen, 1936, 526, 103–115; cf. A., 1932, 1133).—Contrary to previous conclusions, the presence of a substituent vicinal to CO does not prevent the formation of stereoisomeric oximes but diminishes their stability so that it is frequently impossible to obtain the actual derivatives of one form. *cis*- α -Hydrindan-4-one (I) is oximated and benzoylated in $\text{C}_5\text{H}_5\text{N}$ thereby giving the *Bz* derivatives, m.p. 114° and 92–93°, respectively, of the *cis*- α -hydrindan-4-oneoximes, m.p. 57–59° and 77–78°, respectively. The oximes form an equilibrium mixture when heated; neither yields a homogeneous amine when hydrogenated (Pt sponge in AcOH). When distilled at atm. pressure (I) is partly isomerised to *trans*- α -hydrindan-4-one, and oximation of the mixture affords *trans*- α -hydrindan-4-oneoxime, m.p. 163° (*Bz* derivative, m.p. 123°), reduced (Pt sponge in AcOH or Na and EtOH) to a not quite homogeneous amine from which *Bz*, m.p. 167–168°, and *Ac*, m.p. 163°, derivatives are isolated. *cis*- α -Ketodecahydronaphthalene similarly affords the *Bz* derivatives, m.p. 112–113° and 107–108°, respectively, of the *cis*- α -ketodecahydronaphthalene-oximes, m.p. 101–102° and 69–70°, respectively. *o*-cyclohexylcyclohexanoneoxime, m.p. 102°, affords a *p*-nitrobenzoyl derivative, m.p. 85–86°, from which it is regenerated by alkali; it is reduced by Na and EtOH to *trans*-*o*-cyclohexylcyclohexylamine (*Bz* derivative, m.p. 157–158°). Hydrogenation (Pd-C) of *d*-carvone (II), b.p. 100–105°/10 mm., $[\alpha]_D^{20} +61.02^\circ$, gives active and inactive carvomenthone and carvacrol and the ketone mixture is suitable only for the prep. of *l*- (III), m.p. 100–101°, $[\alpha]_D -42.3^\circ$, and *r*-, m.p. 104–105°, -carvomenthoneoxime (*p*-nitrobenzoate, m.p. 55–57°, of the latter). Hydrogenation (PtO_2 in Et_2O) of (II) gives a mixture from which, after oximation, (III) is separated in considerable amount; the non-cryst. residue is transformed by *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ in $\text{C}_5\text{H}_5\text{N}$ into the *p*-nitrobenzoates, m.p. 123–124°, $[\alpha]_D^{20} -31.00^\circ$ in abs. EtOH, and m.p. 83–84°, $[\alpha]_D^{20} -60.3^\circ$ in abs. EtOH, of the *cis*-carvomenthoneoximes (IV), m.p. 64–65°, $[\alpha]_D^{20} -72.5^\circ$ in abs. EtOH, and m.p. 30–31°, $[\alpha]_D^{20} -65.5^\circ$ in abs. EtOH. Reduction of either oxime by Na and EtOH gives an almost homogeneous *cis*-carvomenthylamine (V) (*Bz* derivative, m.p. 153°, $[\alpha]_D^{20} -48.5^\circ$ in abs. EtOH, -45.3° in CHCl_3). (IV) are also obtained from the equilibrium mixture derived by treating (III) with H_2SO_4 or from homogeneous *cis*-carvomenthone derived from (V). (III) exhibits unusual luminosity phenomena during recrystallisation; $[\alpha]$ in EtOH or cyclohexane is dependent on concn. (III) gives a benzoate, m.p. 57–58°, $[\alpha]_D^{20} -69.4^\circ$ in EtOH, 1-naphthoate, m.p. 79–80°, $[\alpha]_D^{20} -29.0^\circ$ in EtOH, *p*-nitrobenzoate, m.p. 78–79°, $[\alpha]_D^{20} -67.9^\circ$ in EtOH, and a 3:5-dinitrobenzoate, m.p. 88–89°, $[\alpha]_D^{20} -63.0^\circ$, from which it is regenerated by NaOH. It is reduced in alkaline solution to *trans*-carvomenthylamine (*Bz*

derivative, m.p. 165°, $[\alpha]_D^{20} +52.2^\circ$) and by H_2 in AcOH containing Pt sponge to a mixture of amines. Distillation of (III) at 142°/12 mm. gives an equilibrium mixture, m.p. 78–94°, from which (III) and a *trans*-carvomenthoneoxime, m.p. 30–32°, $[\alpha]_D^{20} +73.5^\circ$ or $+91.2^\circ$ in EtOH (dependent on c), $[\alpha]_D^{20} +110.9^\circ$ or $+120.3^\circ$ in cyclohexane, are isolated. The latter becomes equilibrated when heated above its m.p. and gives the same *p*-nitrobenzoate as (III).

H. W.

Molecular rearrangement in the cyclic hydrocarbon series. Isomerisation of epoxides derived from 1-benzyl-4-methyl- Δ^1 -cyclohexene and 1-benzylidene-4-methylcyclohexane. M. TIFFENEAU and (MLLE.) J. GUTMAN (Compt. rend., 1936, 203, 797–799; cf. A., 1922, i, 537; 1935, 1240).—1-Benzyl-4-methylcyclohexan-1-ol, b.p. 157–158°/15 mm., and phenyl-4-methylcyclohexylcarbinol, b.p. 165–166°/15 mm., are dehydrated by Al_2O_3 at 300–320°, to 1-benzyl-4-methyl- Δ^1 -cyclohexene (I), b.p. 133°/15 mm., and 1-benzylidene-4-methylcyclohexane (II), b.p. 136–137°/15 mm., respectively; the latter is isomerised partly to the former (cf. A., 1936, 195). Isomerisation of the epoxy-derivative (III) of (I) affords 2-benzyl-5-methylcyclohexanone (IV) (semicarbazone, m.p. 179°) and 1-benzyl-3-methylcyclopentane-1-aldehyde (1-carboxylic acid, m.p. 98–99°) in the ratio 3:1, which indicates that only one C-O linking is ruptured, namely the one involving the C carrying the benzyl group. 2-Benzyl-4-methylcyclohexanone (semicarbazone, m.p. 145–146°) and 1-phenylacetyl-3-methylcyclopentane, b.p. 162°/20 mm. (oxime, m.p. 53°), are prepared (no details given) but are not isolated from the products of polymerisation. The epoxide (V), b.p. 153–154°/20 mm., of (II) when isomerised affords only 1-phenyl-4-methylcyclohexane-1-aldehyde (1-carboxylic acid, m.p. 165–166°) by rupture of the C-O linking involving the *tert*-C. The small amount of (IV) isolated probably arises from (I) present as an impurity in (II).

J. L. D.

Action of organo-magnesium compounds on ketoximes. J. HOCH (Compt. rend., 1936, 203, 799–801; cf. A., 1934, 893).— $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$ with MgMeI at 100° affords $\text{CPh}_2\cdot\text{NH}$ (phenylurethane, m.p. 165°), $\text{CPh}_2\cdot\text{NPh}$, and COPhMe on prolonged heating, but when heated for a short time, NH_2Ph and a base, $(\text{C}_{14}\text{H}_{11}\text{N})_2$, m.p. 210°, are found among the other products. With MgEtBr , NH_2Ph , COPh_2 , and COPhEt are formed. MgPhBr affords *o*-phenylbenzhydriylaniline (cf. A., 1929, 1056). The probable mechanism of these reactions is discussed. J. L. D.

Derivatives of 4-cyclohexyldiphenyl. I. F. R. BASFORD (J.C.S., 1936, 1593–1595).— Ph_2 and cyclohexyl bromide yield with $\text{AlCl}_3\text{-CS}_2$ 4-cyclohexyldiphenyl (I), dehydrogenated by Se to *p*- $\text{C}_6\text{H}_4\text{Ph}_2$ and oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ to *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$, and 4:4'-dicyclohexyldiphenyl (II), dehydrogenated by Se to 4:4'-bisdiphenyl. (II) also results from (I) and cyclohexyl bromide with $\text{AlCl}_3\text{-CS}_2$. (I) yields with AcCl and $\text{AlCl}_3\text{-CS}_2$ 4'-acetyl-4-cyclohexyldiphenyl (III), m.p. 158° (phenylhydrazone, m.p. 172°; semicarbazone, m.p. 270°; oxime, m.p. 196°), and with $\text{BzCl-AlCl}_3\text{-CS}_2$ 4'-benzoyl-4-cyclohexyldiphenyl (IV), m.p. 123° (oxime, m.p. 188°; semicarbazone, m.p.

240°). 4-cyclohexyldiphenyl-4'-dicarboxylic acid, m.p. 288° (Me ester, m.p. 152°), obtained by oxidation of (III) by NaOCl or NaOBr, or by KOH-CaO fusion of (IV), is further oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4\text{-AcOH}$) to diphenyl-4 : 4'-dicarboxylic acid. J. D. R.

Phenanthrene derivatives. V. Beckmann rearrangement of oximes of acetyl- and benzoyl-phenanthrenes. W. E. BACHMANN and C. H. BOATNER (J. Amer. Chem. Soc., 1936, 58, 2097—2101).—Partly a more detailed account of work previously reviewed (A., 1935, 1117; 1936, 836). The mixtures of oximes obtained (using $\text{NH}_2\text{OH}\cdot\text{HCl}$ in $\text{EtOH-C}_6\text{H}_5\text{N}$) from 1-, 2-, 3-, and 9-acetylphenanthrenes contain a large preponderance of the *trans*-forms, since Beckmann rearrangement gives 71, 81, 87, and 50%, respectively, of the acetamidophenanthrenes and, 1, 1, 2, and 6%, respectively, of the phenanthrenecarboxymethylamides; the mixtures are subsequently hydrolysed (EtOH-conc. HCl) and separated as amines and acids. The mixtures of oximes from 1-, 2-, 3-, and 9-benzoylphenanthrenes contain a majority of the *cis*-forms; rearrangement affords 82, 56, 63, and 96%, respectively, of the phenanthrenecarboxylanilides and 18, 44, 37, and 4%, respectively, of the benzamidophenanthrenes. The terms *cis* and *trans* denote the relative positions of the phenanthryl and OH groups. Rearrangement is effected with PCl_5 in C_6H_6 .

1-Phenanthrylmethylcarbinol, m.p. 108—110° [from (II) (below) and MgMeI in $\text{Et}_2\text{O-C}_6\text{H}_6$], is oxidised ($\text{CrO}_3\text{-AcOH}$) to 1-acetylphenanthrene, m.p. 112—113° (*trans-oxime*, m.p. 174—176°), also prepared from 1-cyanophenanthrene (from the amide and P_2O_5 at 140°) and MgMeI in $\text{Et}_2\text{O-C}_6\text{H}_6$. 9-Acetylphenanthrene, m.p. 73—74°, is obtained from the nitrile. The *trans-oxime* of 2-acetylphenanthrene has m.p. 196—197° (cf. Mosettig and Krueger, A., 1936, 1125). 1-Aminophenanthrene, m.p. 145—146° [hydrochloride, m.p. 253—255° (previous decomp.); picrate, m.p. 203—204° (decomp.); Ac, m.p. 219—220.5°, Bz, m.p. 224—226°, and $\text{N-CO}_2\text{Et}$, m.p. 153.5—154°, derivatives], with PhNO in C_6H_6 gives N-phenyl-N'-1-phenanthrylcarbamide, m.p. 325—326° (decomp.). Phenanthrene-1-, -2-, -3-, and -9-carboxymethylamides, m.p. 204—205.5°, 201—202°, 207—207.5°, and 191—192°, respectively, are synthesised from the acid chlorides. 1-, 2-, 3-, and 9-Benzoylphenanthrene oximes, m.p. 185—186°, 182—183°, 201—203°, and 218—220°, respectively, are described. The imino-chloride (I) from phenanthrene-1-carboxylanilide, m.p. 248—249°, is reduced ($\text{SnCl}_2\text{-Et}_2\text{O-HCl}$, $\text{s-C}_2\text{H}_4\text{Br}_2$) to 1-aldehydophenanthrene (II), m.p. 110.5—111.5° (*oxime*, m.p. 187—189°); the crude anilide (from the rearrangement) is actually used. Phenanthrene-1-carboxylic acid is best obtained by hydrolysis (MeOH-conc. HCl followed by MeOH-KOH) of the product from (I) and $\text{Et}_2\text{O-MeOH-NaOMe}$.

H. B.

4 : 5-Dialkyl-substituted 2-aminodiaryl ketones.—See B., 1936, 1143.

Oxidation of hydroxyacetophenone. K. ONO and M. IMOTO (J. Chem. Soc. Japan, 1935, 56, 991—998).—Oxidation of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ with PhNO_2

affords $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$, whilst $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ similarly yields salicylic acid.

CH. ABS. (r)

Fries rearrangement of 4-benzoyloxydiphenyl. L. F. FIESER and C. K. BRADSHAW (J. Amer. Chem. Soc., 1936, 58, 2337—2338; cf. A., 1936, 1374).—4-Benzoyloxydiphenyl (I) is treated with AlCl_3 in CS_2 , the CS_2 removed, and the residue heated at 160°/30 min.; 4-hydroxy-4'-benzoyldiphenyl (II), m.p. 194—195° (acetate, m.p. 127—128°), is isolable in 22% yield from the resulting mixture. The Me ether, m.p. 165—166°, of (II) is also prepared from 4-methoxydiphenyl-4'-carboxyl chloride, C_6H_5 , and AlCl_3 and from $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{OMe}$, BzCl , and AlCl_3 in cold $\text{C}_2\text{H}_2\text{Cl}_4$; in the latter case approx. the same amount of 4-methoxy-3-benzoyldiphenyl, m.p. 91—92°, is also produced. Different results (Blicke and Weinkauff, A., 1932, 273; Hey and Jackson, A., 1936, 991) for the rearrangement of (I) are probably due to variations in experimental procedure.

H. B.

Acylation and alkylation of β -diketones and β -sulphonyl-ketones. E. P. KOHLER and H. A. POTTER (J. Amer. Chem. Soc., 1936, 58, 2166—2170; cf. A., 1936, 335).—The amounts of C- and O-Bz derivatives formed when Cu and MgBr derivatives (which must be prepared and used in Et_2O at low temp. to minimise cleavage reactions) of various β -diketones and β -sulphonyl-ketones containing Ph and/or mesityl groups are treated with BzCl show that acylation is not greatly affected by the metal; the mesityl group promotes O-benzoylation, presumably because of the greater tendency of the $>\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ group to undergo enolisation. The view (cf. Arndt and Martius, A., 1933, 146) that SO_2 groups cannot promote enolisation is considered to be untenable.

The Cu and MgBr derivatives of CH_2Bz_2 with BzCl give 80 and 80.5%, respectively, of CHBz_3 ; the former and BzBr afford 60% of CHBz_3 and 22% of α -benzoyloxy- β -benzoyl- α -phenylethylene, two forms, m.p. 108° and 125°. The MgBr derivative of benzoylmesitylmethane (I) with BzCl yields 65% of dibenzoylmesitylmethane (II) and 18% of an O-benzoate (III), m.p. 91°, of (I); the Cu derivative with BzCl and BzBr gives 60 and 45%, respectively, of (II) and 30 and 30%, respectively, of (III). The Cu and MgBr derivatives of dimesitylmethane with BzCl afford 49 and 96%, respectively, of α -benzoyloxy- β -mesityl- α -mesitylethylene, m.p. 136°; C-benzoylation does not occur. The MgBr derivative of Ph *p*-toluenesulphonylmethyl ketone (IV) and BzCl give 81% of dibenzoyl-*p*-toluenesulphonylmethane (V), m.p. 196°, whilst the MgBr derivative of mesityl *p*-toluenesulphonylmethyl ketone (VI), m.p. 180° [from $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Na}$, and a little EtOH at 100° (sealed tube) for 75 hr.], similarly affords 16% of benzoylmesityl-*p*-toluenesulphonylmethane, m.p. 147°, and 64% of α -benzoyloxy- β -*p*-toluenesulphonyl- α -mesitylethylene, two forms, m.p. 120° and 126°. Benzoyldi-*p*-toluenesulphonylmethane (VII) is obtained in 80% yield from $(p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2)_2\text{CH}\cdot\text{MgBr}$ and BzCl , whilst mesityl-dibenzenesulphonylmethane (80%) is formed from $(\text{PhSO}_2)_2\text{CH}\cdot\text{MgBr}$. The MgBr derivatives of (V),

and (VII) with BzCl give α -benzoyloxy- β -benzoyl- β -p-toluenesulphonyl- α -phenylethylene (96%), m.p. 166°, and α -benzoyloxy- β -di-p-toluenesulphonyl- α -phenylethylene, respectively; the former with p-C₆H₄Br·COCl affords a p-bromobenzoyl derivative, C₂₉H₂₁O₅SBr, m.p. 189°, which differs from the Bz derivative, two forms, m.p. 182° and 201°, obtained from BzCl and the MgBr derivative of benzoyl-p-bromobenzoyl-p-toluenesulphonylmethane, m.p. 212° [from (IV)], thus establishing that the above O-Bz derivatives are not tetra-acylmethanes.

p-C₆H₄Me·SNa and CPh·CH₂Cl in MeOH give Ph p-toluenesulphonylmethyl ketone, b.p. 182—184°/5 mm., m.p. 46°, oxidised (H₂O₂) to (IV). (VI) and CH₂N₂ in cold C₆H₆ afford α -methoxy- β -p-toluenesulphonyl- α -mesitylethylene, m.p. 137° [also obtained from the Na derivative of (VI) and Me₂SO₄ in C₆H₆], which when heated at 130°/vac. for 6 hr. passes into an isomeride, m.p. 147° [also prepared from the MgBr derivative of (VI) and Me₂SO₄ in C₆H₆]; both ethers are hydrolysed (HCl) to (VI). (VI) and MeI in MeOH-NaOMe give α -mesitoyl- α -p-toluenesulphonylethane, m.p. 171°. Tribenzoylmethyl chloride, m.p. 122° (from CHBz₃ and Cl₂ in CHCl₃), is reduced by p-C₆H₄Me·SO₂Na to CHBz₃, and reacts with p-C₆H₄Me·SNa in C₆H₆ to yield CNaBz₃ and (p-C₆H₄Me·S)₂. H. B.

Synthesis of phenanthrene and hydrophenanthrene derivatives. VI. 1':3'-Diketocyclopentenophenanthrenes. L. F. FIESER, M. FIESER, and E. B. HERSHBERG (J. Amer. Chem. Soc., 1936, 58, 2322—2325).—Phenanthrene-1:2- and -3:4-dicarboxylic esters condense smoothly with EtOAc in presence of Na to give diketocyclopentenophenanthrenes. Me phenanthrene-1:2-dicarboxylate, two forms, m.p. 131.8—132.2° (pale yellow) and 132.5—133° (colourless), the former obtained from the 1:2-anhydride (A., 1935, 1495) and MeOH-HCl and both from the K₂ salt and MeOH-HCl, with EtOAc + Na followed by hydrolysis (EtOH-conc. HCl) gives 1':3'-diketo-1:2-cyclopentenophenanthrene (I), m.p. 240.5—241.5° (decomp.). Phenanthrene-3:4-dicarboxylic anhydride, m.p. 253.5—254° [obtained by dehydrogenation (S at 320—330°) of its 1:2-H₂-derivative (*loc. cit.*)], and MeOH-HCl afford Me phenanthrene-3:4-dicarboxylate, m.p. 114.5—114.8° [also prepared from the free acid (+H₂O) and CH₂N₂], which gives (as above) 1':3'-diketo-3:4-cyclopentenophenanthrene (II), m.p. 201.4—202° (semicarbazone, decomp. 300—305°). Me 8:9-acephenanthrene-1:2-dicarboxylate, m.p. 170.6—171° [from the 1:2-anhydride, m.p. 297—298° (uncorr.)], similarly yields 1':3'-diketo-1:2-cyclopenteno-8:9-acephenanthrene, m.p. 338—340° (uncorr.) (decomp.). (I) and (II) dissolve in cold dil. alkali to red solutions. (II) heated with N-NaOH undergoes fission to 4-acetylphenanthrene-3-carboxylic acid, m.p. 201.5—202.5°, decarboxylated (basic Cu carbonate in quinoline) to 4-acetylphenanthrene, m.p. 89.8—90.3° (picrate, m.p. 129.5—130.5°), which is oxidised (NaOCl) to phenanthrene-4-carboxylic acid, m.p. 171.5—173°. (I) is similarly cleaved to a mixture of acetylphenanthrenecarboxylic acids. Me 3:4-dihydrophenanthrene-1:2-dicarboxylate has m.p. 109.8—110°. All m.p.

are corr. unless stated otherwise. (I) possesses oestrogenic activity of the same order as 1-keto-1:2:3:4-tetrahydrophenanthrene; (II) is inactive.

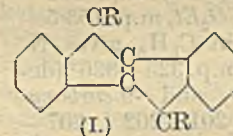
H. B.

Complex salts of phenylhydrazono-oximes [of diketones] and of phenanthraquinone-mono- and -di-oxime. W. CIUSA (Gazzetta, 1936, 66, 591—597).—The phenylhydrazono oxime of Ac₂ forms Ni, decomp. 225°, and Co salts, and that of Bz₂ Ni, decomp. 240°, and Co salts. Phenanthraquinone-oxime gives Ni and Co salts, and forms with FeSO₄ a green salt, and with FeCl₃ a red salt; it is a sensitive reagent for Co and Fe. The dioxime gives Ni and Co salts, and salts with FeSO₄ and FeCl₃.

E. W. W.

Rearrangement of 5-benzoyl-1-phenyl- Δ^1 -cyclopentene oxide. S. H. BABCOCK, jun., and R. C. FUSON (J. Amer. Chem. Soc., 1936, 58, 2325—2326).—The oxide (I) (modified prep.; cf. A., 1934, 1005) is converted by short treatment with EtOH-HCl into 3-benzoyl-2-phenylcyclopentanone (II), m.p. 159—159.5° (corr.) (Br₂-derivative, m.p. 136.5—137.5°), the 5-p-chlorobenzylidene derivative, m.p. 207—207.5°, of which is oxidised (O₃) to p-C₆H₄Cl·CHO, p-C₆H₄Cl·CO₂H, and β -benzoyl- α -phenylglutaric anhydride, m.p. 183—184° (free acid, two forms, m.p. 135—136° and 176—177°; the latter isomerises to the former when heated with 6% EtOH-KOH). (I) is also rearranged under defined conditions by hot AcOH to (probably) the geometrical isomeride, m.p. 123.5—124.5°, of (II) (*cf. loc. cit.*). H. B.

Diphenysuccindene series. XIV. Derivatives of Δ^{10} -diphenysuccindene. K. BRAND, W. GABEL, and H. ÖTT [with, in part, K. O. MÜLLER and R. FLEISCHHAUER]. XV. 10-Amino-derivatives of diphenysuccindan-9:12-dione. K. BRAND and H. ÖTT (Ber., 1936, 69, [B], 2504—2514, 2514—2520).—XIV. Gradual addition of p-NO·C₆H₄·NMe₂ to Δ^{10} -diphenysuccindene in NaOEt-EtOH at 50—60° gives Δ^{10} -diphenysuccindene-9:12-dione-di-p-dimethylamino-anil (I) (R = :N·C₆H₄·NMe₂), m.p. 274—277.5° according to the manner of heating, converted by NH₂OH·HCl in boiling EtOH-H₂O into Δ^{10} -diphenysuccindene-9:12-dione-dioxime, m.p. 272°, and transformed by 0.1N-HCl-C₆H₆ at room temp., 5% HCl-EtOH, or boiling 2N-HCl into CO and a red compound (II), C₃₁H₁₆O₃, m.p. 284°, in place of the expected dione. Gradual addition of Br in CCl₄ to a boiling solution of diphenysuccindan-9:12-dione (III) in CCl₄ exposed to ultra-violet light gives 10-bromodiphenysuccindan-9:12-dione (IV), m.p. 147°, reduced by Zn dust in boiling EtOH or H₂-ZnO-Pd in EtOH to (III) and converted by NaOAc in boiling EtOH into (II) and CO. (II) is most readily obtained by addition of SeO₂ to (III) in boiling AcOH.



XV. (IV) in boiling EtOH with NH₃, NH₂Me, NHMe₂, or NHEt₂ gives small amounts of (II), but mainly colourless or orange substances which could not be obtained homogeneous. C₆H₅N yields mainly (II) whereas with piperidine a N-containing compound, m.p. 166.5°, of unexplained structure is also produced. Gradual addition of cyclohexylamine

to (IV) in boiling EtOH yields (II) whereas 10-cyclohexylaminodiphensuccindan-9:12-dione, m.p. 141°, is formed if an immediate excess of the reagent is used. Under similar conditions, hexahydro-*o*-toluidine appears to yield impure (III). With aromatic amines (except α -C₁₀H₇·NH₂ and NHPh₂) (IV) readily yields the corresponding yellow 10-arylaminodiphensuccindan-9:12-diones, transformed by protracted boiling with mineral acids (preferably conc. H₃PO₄ and AcOH) into (II). The following individuals are described: 10-anilino-, m.p. 202.5° (hydrochloride, m.p. 210—211°); 10-*o*-toluidino-, m.p. 167.5°; 10-*m*-toluidino-, m.p. 191.5°; 10-*p*-toluidino-, m.p. 180.5°; 10-*o*-, m.p. 169°, 10-*m*-, m.p. 187° [which does not yield (II)] and 10-*p*-, m.p. 145.5°, -methoxyanilino-; 10-*o*-, m.p. 179°, 10-*m*-, m.p. 175.5° [which does not yield (II)], and 10-*p*-, m.p. 135°, -ethoxyanilino-; 10- β -naphthylamino-, m.p. 173°. H. W.

Enol-acetates from progesterone and testosterone. U. WESTPHAL (Naturwiss., 1936, 24, 696—697).—Progesterone (I) with Ac₂O and AlCl₃ affords a monoenol-acetate, m.p. 138° (1 rabbit unit = about 1.2 mg.), which is hydrolysed (dil. H₂SO₄-EtOH) to (I). Testosterone (II) similarly affords a dienol-acetate, m.p. 155° (1 capon unit = 0.125 mg.; when tested on the castrated mouse, 2 mg. are inactive), hydrolysed to (II). J. L. D.

Adrenal cortex. II. Identification of a substance having the qualitative action of cortin; its conversion into a diketone closely related to androstenedione. H. L. MASON, C. S. MYERS, and E. C. KENDALL (J. Biol. Chem., 1936, 116, 267—276).—Compound-*E* (I) isolated from the extract of the adrenal gland (A., 1936, 1117) is actually C₂₁H₂₈O₅ and contains 3 OH and 2 CO. Oxidation of (I) with HIO₄ gives CH₂O and acid-5 (A; R = OH, R' = CO₂H), darkens 250°, m.p. 263—265° (decomp.), oxidised by K₂Cr₂O₇-N·H₂SO₄-COMe₂ to ketone-4 (II) (A; RR' = :O), m.p. 214—217° (decomp.) [2:4-dinitrophenylhydrazones, m.p. 254—256° (decomp.)], also obtained by similar direct oxidation of (I). (I) is unchanged in solution between *p*_H 2.5 and 8, but with 1 mol. of NaOH it is converted into an acid. Since (I) exhibits qualitatively the same physiological action (adrenalectomised rats) as cortin, and (II) has approx. 25% of the activity of androsterone in the capon test, the presence of the sterol ring system in *E*, and by implication in cortin, is highly probable and the structure (A) (R = OH; R' = CO·CH₂·OH) is proposed for (I). Analysis of its 2:4-dinitrophenylhydrazone, m.p. 270° (decomp.), confirms the formula C₂₀H₂₆O₄ assigned to acid-1 (absorption max. 2380 Å.) (loc. cit.). J. W. B.

Composition of buds of *Populus balsamifera*.—See A., III, 50.

Constituent of *Drosera rotundifolia*. H. DIETTERLE and E. KRUTA (Arch. Pharm., 1936, 274, 457—461).—Plumbagin (I) from (*D. rotundifolia*) with alkaline H₂O₂ followed by methylation gives 3:1:2-OMe·C₆H₃(CO₂H)₂. 5:6:1-NO₂·C₁₀H₅Me·NH₂ and

HNO₂ give 5:6:1-NO₂·C₁₀H₅Me·OH, m.p. 157—158°, and thence (Zn-HCl) 5-amino-6-methyl- α -naphthol hydrochloride, which with H₂O₂-AcOH gives 5-hydroxy-2-methyl- α -naphthaquinone, identical with (I), m.p. 77°. Droserone is identical with (I) and this name should be abandoned. R. S. C.

Nitrogenous derivatives of hydroxyanthraquinone glucosides. II. Theory of sugar absorption by hydroxyanthraquinones. S. MÜLLER (Magyar chem. Fol., 1935, 41, 9—18; Chem. Zentr., 1936, i, 557).—1:2- and 1:8-Dihydroxyanthraquinone glucosides with NH₃ yield NH₂-derivatives; the reaction is facilitated by the sugar residue.

H. N. R.

[Interaction of] aldehydes and 1-nitro-2-methylantraquinone. M. BATTEGAY and G. MANGENEY (Compt. rend., 1936, 203, 792—794).—PhCHO with 1-nitro-2-methylantraquinone (I) in PhNO₂ containing piperidine at 110° affords 1-nitro-2-styrylantraquinone (+ piperidine). *p*-NMe₂·C₆H₄·CHO similarly gives 1-nitro-2-*p*-dimethylaminostyrylantraquinone, m.p. 290° [sulphate; easily reduced (Na₂S) to the NH₂-compound (Bz derivative); and Br₂ additive compound], and some NMe₂·C₆H₄·CH(CH₂·C₁₄H₉O₂·NO₂)₂, m.p. 269°, which does not react with Br, but with Na₂S affords the (NH₂)₂-compound. J. L. D.

Preparation of chlorobenzamidoanthraquinones.—See B., 1936, 1197.

Constitution of perillene. H. KONDO and H. SUZUKI (Ber., 1936, 69, [B], 2459—2473).—Perillene (I), obtained from the essential oil of *Perilla citriodora*, Makino, after removal of much citral, has b.p. 93°/25 mm., 185—186°/760 mm. It is hydrogenated (Pt-black in AcOH; 760 mm.) to dihydroperillene (II), b.p. 182°, by Pd in AcOH to hexahydroperillene (III), b.p. 86—87°/13 mm., and by PtO₂ in AcOH (2.5 atm.) to octahydroperillene (IV), b.p. 90—91°/4 mm., 212—213°/760 mm. Oxidation of (IV) by CrO₃ in AcOH at 70—80° gives ϵ -methyl- α -ethyl-*n*-heptioic acid, b.p. 119°/4 mm. (corresponding chloride, b.p. 61°/1.5 mm., amide, m.p. 88°, and anilide, m.p. 67°), obtained synthetically from Et₂ ethylisohexylmalonate, b.p. 119—120°/3 mm., and ethylisohexylmalonic acid, m.p. 102°. Oxidation of (III) in aq. suspension by KMnO₄ at 100° affords H₂C₆O₄ and δ -methylamylsuccinic acid, m.p. 78°, proving that a substituent is not present at 2 or 5 in the furan nucleus of (I), and that (IV) is ζ -methyl- β -ethylheptanol. Similar oxidation of (II) gives δ -methyl-*n*-hexoic acid (anilide, m.p. 77°; *p*-bromophenacyl, m.p. 76—77°, and *p*-phenylphenacyl, m.p. 77°, esters). Oxidation of (I) with KMnO₄ yields AcOH and (CH₂·CO₂H)₂, whilst ozonisation followed by reductive fission of the ozonide gives COMe₂, (CH₂·CO₂H)₂, and CHO·[CH₂]₂·CO₂H (2:4-dinitrophenylhydrazone, m.p. 201°). (I) is therefore 3- δ -methyl- Δ^7 -pentenylfuran. Its possible conversion into or formation from citral is discussed. The following observations are incidental. Et₂ *n*-propylisoamylmalonate, b.p. 135—137°/4 mm., from CHPr^a(CO₂Et)₂ and isoamyl bromide or by propylation of Et₂ isoamylmalonate, is converted successively into *n*-propylisoamylmalonic acid, m.p. 150°, and δ -methyl- α -*n*-propyl-*n*-hexoic acid, b.p. 117—119°/4

mm. (corresponding *chloride*, b.p. 83—84°/4 mm., *amide*, m.p. 118°, and *anilide*, m.p. 87·5°). Et_2 *isoheptylmalonate* and MeI afford Et_2 *methylisoheptylmalonate*, b.p. 140—145°/4 mm., whence *methylisoheptylmalonic acid*, m.p. 126°, and $\alpha\zeta$ -*dimethyl-n-octioic acid*, b.p. 114—117°/2 mm. (corresponding *chloride*, b.p. 75°/1·5 mm., *amide*, m.p. 93·5°, and *anilide*, m.p. 93°). ϵ -Iodo- β -methylhexane, Na , and $\text{CH}_2(\text{CO}_2\text{Et})_2$ in EtOH yield Et_2 $\alpha\delta$ -*dimethylamylmalonate*, b.p. 130—135°/4 mm., whence Et_2 *methyl- $\alpha\delta$ -dimethylamylmalonate*, b.p. 113—116°/2 mm., *methyl- $\alpha\delta$ -dimethylamylmalonic acid*, m.p. 117—118°, and $\alpha\beta\epsilon$ -*trimethyl-n-heptioic acid*, b.p. 120°/3 mm., 240°/760 mm. (corresponding *chloride*, b.p. 50—52°/1 mm., and *amide*, m.p. 109—110°). *Ethylisoamylcarbinol*, from $\text{CH}_3\text{Bu}^t\text{Br}$ and EtCHO , is transformed by P and Br into γ -*bromo- ζ -methylheptane*, b.p. 179—185°, which gives Et_2 δ -*methyl- α -ethylamylmalonate*, b.p. 119—124°/4 mm., whence ϵ -*methyl- β -ethyl-n-heptioic acid*, b.p. 120—121°/4 mm. (corresponding *chloride*, b.p. 90—91°/15 mm., *amide*, m.p. 56°, and *anilide*, m.p. 50—51°). H. W.

Phellandrenes. III. Correlation of l - α -phellandrene with l -4-isopropyl- Δ^2 -cyclohexen-1-one. A. S. GALLOWAY, J. DEWAR, and J. READ (J.C.S., 1936, 1595—1597).—Crude l -4-isopropyl- Δ^2 -cyclohexen-1-one (2:4-dinitrophenylhydrazone, m.p. 129—130°) is reduced [$\text{Al}(\text{OPr}^i)_3$ - Pr^iOH] to a mixture from which the corresponding *alcohol*, b.p. 97°/8 mm. [α]_D -139·3° in EtOH [3:5-dinitrobenzoate, m.p. 115°, [α]_D -136·5° in CHCl_3 ; *p*-nitrobenzoate, m.p. 84°, [α]_D -168·5° in CHCl_3], is isolated. The *alcohol* is re-oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$) to the pure *ketone*, b.p. 90°/9 mm., [α]_D -119·3° in EtOH . The crude *ketone* and MgMeI yield l - Δ^2 -menthen-1-ol, b.p. 92°/11 mm., [α]_D -61·2° in EtOH , converted by heating with $\text{H}_2\text{C}_2\text{O}_4$ into l - α -phellandrene. Possible modes of derivation of the *ketone* in nature are discussed.

F. R. S.

Piperitone. XIII. Polymorphism of benzylidene- dl -piperitone and some analogues. J. DEWAR, D. R. MORRISON, and J. READ (J.C.S., 1936, 1598—1600).— γ -Benzylidene- dl -piperitone, m.p. 69—70°, has been obtained, into which pass both the α - and β -forms, previously prepared; the γ - cannot be reconverted into the α - or β -form. Lack of dimorphism is shown by *p*-dimethylaminobenzylidene-, m.p. 116—117°, and *furfurylidene- dl -piperitone*, m.p. 66°. *Hydroxymethylene-*, b.p. 120—122°/14 mm., with NH_2Ph affords *anilinomethylene-*, m.p. 103°, and β -*naphthylaminomethylene- dl -menthone*, m.p. 58—61°, which are not dimorphous. Dimorphous forms of *m*- (α -, m.p. 161°, and labile β -forms, m.p. 110°) and *p*-nitroanilinomethylene- dl -menthone (α -form, m.p. 147°, and β -form, m.p. 117°) have been obtained. *m*-Nitroanilinomethylene- l -menthone, m.p. 104°, does not exhibit dimorphism or mutarotation. F. R. S.

Properties of pine balsam obtained under the stimulating influence of hydrochloric acid. M. HESSENLAND, G. STEPHANI, and M. LEO (Ber., 1936, 69, [B], 2473—2482).—A balsam obtained from *Pinus silvestris* without use of HCl contained turpentine 23·2%, crude resin 71·5%, and H_2O 4·6% in comparison with 23·4%, 70·4%, and 5·7% when

HCl was used. The turpentines are very closely similar to one another. The resin acids obtained from "stimulated" balsam resemble those of the untreated product in m.p. but are considerably less laevorotatory. Apparently HCl is present in sufficient amount to cause the preliminary diminution of $[\alpha]$ which is the first stage in the transformation of resin acids into (—)-abietic acid under the influence of mineral acid.

H. W.

Pinene hydrochloride. H. MEERWEIN and J. VORSTER (J. pr. Chem., 1936, [ii], 147, 83—92).—Pure pinene (I) and HCl in low-boiling ligroin at -60° to -70° in complete absence of H_2O give a product, m.p. between -25° and -5° according to the purity, containing true pinene hydrochloride (II) (70%), bornyl chloride (20—25%), limonene hydrochloride (5—7%), and a little (I). Pure (II) is stable at -60° , but at higher temp., e.g., -25° , varying according to the purity, changes exothermally (temp. rises, e.g., to 25° in 10 min. and then suddenly to $68·5^\circ$) into HCl and bornyl chloride (III); this change is catalysed even at low temp. by H_2O , SnCl_4 , or EtOH , and its rate at higher temp. is greatly influenced by the solvent; thus much Et_2O completely stabilises (II) in EtOH and the free HCl can then be titrated by NaOEt . *k*, approx. unimol., for the decomp. of (II) at 0° is very low in Et_2O , 0·0096 in ligroin, 0·1024 in PhMe , 5·28 in PhCl , and 0·995 in PhOMe . The Cl in (II) is not replaced by OH by means of moist Ag_2O . The decomp. of (II) in aq. NaCl at -20° is stopped by a small excess of NaOH and greatly accelerated by H^+ . These facts and the close parallelism with camphene hydrochloride exclude the possibility that (II) is a mol. compound of (I) and HCl and prove its structure. R. S. C.

Synthetic preparation of β -(or 10)-hydroxycamphor.—See B., 1936, 1234.

Camphor series. III. Tautomeric behaviour of thiocamphor and the activity of its sodium derivative. D. C. SEN (J. Indian Chem. Soc., 1936, 13, 523—526).—Thiocamphor (I) with NaNH_2 followed by aldehydes yields benzylidene-, m.p. 105° (*oxime*, m.p. 200°), and *p*-methoxy-, m.p. 118° (*oxime*, m.p. 171°), *p*-dimethylamino- (prep. using Na), m.p. 91°, and *o*-nitro-benzylidene- dl -thiocamphor, m.p. 135° (*oxime*, m.p. 199°). The Na derivative of (I) with MeI yields *S*-methylthiocamphor [3-methylthiolbornylene], b.p. 85—88°/12 mm., hydrolysed by H_2SO_4 at 150° to camphor and MeSH ; similarly *S*-ethylthiocamphor, b.p. 105°/8 mm., yields EtSH . Benzylidene- dl -camphor *oxime*, m.p. 200°, and *p*-methoxybenzylidene- dl -camphor, m.p. 101° (*oxime*, m.p. 171°), are also prepared. E. W. W.

Lanceol, a sesquiterpene alcohol from the oil of *Santalum lanceolatum*. I. A. E. BRADFELD, E. M. FRANCIS, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1936, 1619—1625).—Lanceol (I), $\text{C}_{15}\text{H}_{24}\text{O}$, b.p. 175—176°/17 mm., [α]_D²⁵ -77·4°, gives an *allophanate*, m.p. 114—115°, and a *strychnine salt*, m.p. 103—105°, is monocyclic, and has three ethylenic linkings which cannot be conjugated. Oxidation with H_2CrO_4 affords in poor yield an aldehyde, $\text{C}_{15}\text{H}_{22}\text{O}$, b.p. 165—175°/15 mm. (*semicarbazone*, m.p. 151—152°; *p*-nitrophenylhydrazone, m.p. 135—

136°), and with O_3 gives CH_2O , hydroxyacetone, and an oil, which with Ag_2O affords lævulic acid (*phenyl-semicarbazone* of Me lævulate, m.p. 115°), and an acid (II), $C_9H_{12}O_4$, m.p. 174° (*di-p-phenacyl ester*, m.p. 105—106°). (II) on oxidation (O_3) forms δ -acetylbutane- $\alpha\beta$ -dicarboxylic acid. Et 3-carbethoxy-1-methylcyclopentan-2-one-3-acetate, b.p. 173—175°/19 mm., is hydrolysed to 1-methylcyclopentan-2-one-3-acetic acid (*semicarbazone*, m.p. 175—176°; *phenyl-semicarbazone*, decomp. 175—176°; Me ester, b.p. 123°/20 mm.). The Me ester with HCN forms Me 2-hydroxy-2-cyano-1-methylcyclopentane-3-acetate, b.p. 166°/20 mm., which with $SOCl_2$ yields a nitrile hydrolysed to 1-methyl- Δ^1 -cyclopentene-2-carboxylic-3-acetic acid, m.p. 200—202°, not identical with (II), and 2-cyano-1-methyl- Δ^1 -cyclopentene-3-acetic acid, decomp. 216°.

Et hexane- $\alpha\beta\gamma$ -tricarboxylate, b.p. 188°/18 mm., with Na affords Et 1-methylcyclohexan-2-one-3:4-dicarboxylate, b.p. 185°/30 mm., hydrolysed to 1-methylcyclohexan-2-one-4-carboxylic acid, m.p. 85—90° (Me ester, b.p. 132°/21 mm.). The Me ester is converted into Me 2-hydroxy-2-cyano-1-methylcyclohexane-4-carboxylate, b.p. 191°/25 mm., dehydrated and hydrolysed to 2-cyano-p-toluic acid, m.p. 162—163°, and the -amide, decomp. 285°, and 1-methyl- Δ^1 -cyclohexene-2:4-dicarboxylic acid, m.p. 193—195°, not identical with (II). The structures $CMe:CH > C < CH_2 \cdot CMe:CH_2$ for (I) and $CH_2 \cdot CH_2 > C < CH_2 \cdot CH:CMe \cdot CH_2 \cdot OH$ for (I) and $CMe:CH > C < CO_2H$ (II) are tentatively assigned.

F. R. S.

β -Myrcene. Catalytic hydrogenation. G. DUPONT and V. DESREUX (Compt. rend., 1936, 203, 733—736; cf. A., 1936, 1514).—Contrary to expectation, the hydrogenation of β -myrcene (I) by Na-EtOH reduction or by catalytic methods (using 1 mol. of H_2) proceeds both by 1:4 addition and by saturation of the *sec.-tert.* terminal ethylenic linking, giving $CMe_2:CH \cdot [CH_2]_2 \cdot CMe:CHMe$ (II) and $CMe_2:CH \cdot [CH_2]_2 \cdot CEt \cdot CH_2$ (III), respectively. (II) is stable to further hydrogenation and (III) affords tetrahydromyrcene [β -dimethyl- Δ^8 -octene], b.p. 65—66°/17 mm. With Na-EtOH the yield of (III) is small, but with Raney Ni catalyst 37% and with Pd-charcoal 25% is obtained; with Adams Pt-C catalyst, a mixture of (I) and (IV) is obtained which on further hydrogenation gives only (IV).

R. F. P.

Polyterpenoids and their glucosides. III. A_1 - and A_2 -Barrigenol. IV. A_1 -Barrigenol and its crystalline acyl derivatives. V. A_1 -Barrigenol. (2) Acetyl- A_1 -barrigenol and its acyl derivatives. VI. Saponin from the bark of *Schima kankaoensis*, Hay. T. NOZOE and T. KINUGASA (J. Chem. Soc. Japan, 1935, 56, 689—703, 704—714, 864—872, 883—893).—III. A -Barrigenol with dil. alkali affords tiglic acid and A -barrigenol, m.p. 284—285°, the α -acetate (I), m.p. 272—272.5°, of which is further hydrolysed to A_1 -barrigenol, $C_{31}H_{52}O_5$ (?), m.p. 294—295°, which is neutral and unsaturated. In the prep. of (I), A_2 -barrigenol, $C_{31}H_{52}O_6$, m.p. 277—279°, is also obtained.

IV. The following derivatives of A_1 -barrigenol

are described: α -, m.p. 271—272°, β -, m.p. 234—235°, *tetra*-, m.p. 272—273°, and *tris*-, m.p. 227—228°, -*p*-bromobenzoates; *tetra*-, m.p. 182°, and *penta*-, m.p. 272.5°, -acetates; *tetrabenzoate*, m.p. 251—252°; *tetra*-2:4-dinitrobenzoate, m.p. 252—253°.

V. The structure of A_1 -barrigenol is discussed; the partial formula $C_{30}H_{45}(OH)_5$ with a 1:2- or 1:3-*cis*-diol grouping, is suggested.

VI. *K*-Schimanol and schimanogel, m.p. 293—294° (acetate, m.p. 270°), isolated from the bark, show no m.p. depression with A_1 -barrigenol and its penta-acetate, respectively. CH. ABS. (r)

Treatment of pine wood with dioxan and the composition of natural lignin. I. N. I. NIKITIN and I. M. ORLOVA (Ber., 1936, 69, [B], 2434—2438).—Treatment of pine wood with dioxan containing 0.12—0.75% of HCl at 100° gives 16—23.7% of crude lignin (I) pptd. from the solution by Et_2O . In elementary composition and OMe content (I) approximates closely to Willstätter's lignin. Boiling H_2O removes about 37.6% of (I). In the aq. extract of (I) or in the hydrolysate of (I) with boiling 5% H_2SO_4 reducing sugars are present to the extent of 6—8%. According to the method of prep. and the degree of desiccation (I) dissolves completely or to the extent of 75—80% in Schweitzer's reagent and is pptd. as brown flocks on acidification. Its solubility differs completely from that of carbohydrates in the reagent since it is also sol. in $NH_3 \cdot H_2O$. (I) contains 16% of pentosans. The observations are not in agreement with Hilpert's hypothesis (A., 1934, 1205) that lignin is a product of the resinification of very susceptible methylated carbohydrates of wood. H. W.

Relationships between lignin and the hemicelluloses. II. N. I. NIKITIN, M. AVIDON, and I. M. ORLOVA (Ber., 1936, 69, [B], 2439—2443).—Treatment of cotton cellulose with 42% HCl at -12° does not cause complete hydrolysis after 2 hr.; it is therefore improbable that Hilpert's "methylated glucose anhydride" is homogeneous. Pine sawdust is extracted successively with cold *N*-NaOH, Schweitzer's reagent, and boiling MeOH. Very little material passes into the NaOH or MeOH. The portion sol. in Schweitzer's reagent is not completely pptd. by acid; it contains small amounts of OMe. Comparison of the elementary composition and OMe content of the undissolved residue (50%) and the original wood shows that the latter contains a substance (lignin) with <62% of C, which much exceeds that of a carbohydrate or Hilpert's product. Beech sawdust is extracted with H_2O and Et_2O and then with dioxan containing 0.12% of HCl at 100°; addition of Et_2O to the extract ppts. crude lignin (I) which when extracted with boiling H_2O leaves a residue the composition of which is very closely similar to that of the material obtained by use of 42% HCl at room temp. The products removed from (I) by boiling H_2O are mainly carbohydrates, the depolymerisation products of which are pptd. by Et_2O from dioxan. They contain 47.8% of pentosans and differ relatively little in composition from the carbohydrates; 10.8% of OMe is present. H. W.

Constituents of resins. IX. Resin alcohols of mistletoe. K. H. BAUER and U. GERLOFF (Arch. Pharm., 1936, 274, 473—485).—Passage of NH_3 into an Et_2O solution of an Et_2O extract (I) of mistletoe ppts. NH_4 oleolate and gives a resin, which after boiling with KOH yields to ligroin a mixture, m.p. 165—166°, separable by way of the acetates, m.p. 241° and 213°, $[\alpha]_D^{20} +80.2^\circ$ and $+42.8^\circ$ in CHCl_3 , respectively, into α -, m.p. 200°, $[\alpha]_D^{20} +85.3^\circ$ in CHCl_3 (benzoate, m.p. 240°), and β -viscol (II), $\text{C}_{30}\text{H}_{49}\cdot\text{OH}$, m.p. 217°, $[\alpha]_D^{20} +55.7^\circ$ in CHCl_3 (benzoate, m.p. 257°). These sec. alcohols give a colour with $\text{C}(\text{NO}_2)_4$, but are stable to KMnO_4 , are oxidised by CrO_3 (1.3 O) in warm AcOH to α -, m.p. 181° (oxime, m.p. 256°; semicarbazone, m.p. 245°), and β -viscone, $\text{C}_{30}\text{H}_{48}\text{O}$, m.p. 174° (oxime, m.p. 268°; semicarbazone, m.p. 220°), respectively, and are dehydrated (β -more rapidly) to α -, m.p. 169°, $[\alpha]_D^{20} +120.2^\circ$ in CHCl_3 , and β -viscene, m.p. 161°, $[\alpha]_D^{20} +32.2^\circ$ in CHCl_3 , respectively, which absorb (Pd-BaSO₄; EtOAc) 1 H_2 to yield α -, m.p. 98°, and β -viscene, m.p. 136° [both are unsaturated, giving colours with $\text{C}(\text{NO}_2)_4$], respectively. (II) differs from oleanol in spite of resemblances of the alcohols and their derivatives. (I) contains also fatty acids. R. S. C.

Constitution of resin phenols and their biogenetic relationships. III. Constitution of the aromatic groups in pinoresinol. IV. Molecular symmetry of pinoresinol and eudesmin. H. ERDTMAN (Svensk Kem. Tidskr., 1936, 48, 230—235, 236—241).—III. Pinoresinol (I) is converted by NaOH- Et_2SO_4 , or by EtI on a suspension of its K derivative in EtOH, into its Et_2 ether (II), m.p. 122—123° [Br_2 -derivative (III), m.p. 143—144°], which with boiling KMnO_4 gives a 35% yield of vanillic acid Et ether. (III) with HNO_3 (d 1.41) at 50—60° affords only an 18% yield of 5-bromo-4-nitroguaiacol Et ether (IV), m.p. 122—123°, identical with a specimen synthesised thus: vanillin Et ether (2:4-dinitrophenylhydrazone, m.p. 213—215°) with Br-AcOH gives its 6-Br-derivative, m.p. 111—112° (2:4-dinitrophenylhydrazone, m.p. 246—248°), oxidised by hot 4% KMnO_4 to 6-bromovanillic acid Et ether, m.p. 171—172°, converted by heating with conc. HNO_3 into (IV). (II) with AcOH- HNO_3 (d 1.41) at 15—20° gives its $(\text{NO}_2)_2$ -derivative (V), m.p. 195—196°, and a 62% yield of 4-nitroguaiacol Et ether, thus proving that both aromatic rings in (I) are of the vanillin type. With hot conc. HNO_3 either (II) or (V) gives 4:5-dinitroguaiacol Et ether.

IV. (I) with 2N-NaOH and insufficient Me_2SO_4 or Et_2SO_4 gives the (alkali-insol.) dialkyl derivative and a (sol.) mixture of unchanged (I) and the monoalkyl derivative, separated by fractional crystallisation of their benzoates to give, respectively, the Me_1 ether benzoate, m.p. 110—111°, and the Et_1 ether benzoate, m.p. 121—122°. Debenzoylation of either and subsequent appropriate alkylation affords the same Me Et ether, m.p. 75—76°, $[\alpha]_D^{25} +100^\circ$ in C_6H_6 , and its $(\text{NO}_2)_2$ -derivative, m.p. 183—184° (sinters 176—179°), $[\alpha]_D^{25} -122^\circ$ in CHCl_3 . (I) must therefore possess a symmetrical structure, and the stereochemistry of possible structures is briefly discussed. J. W. B.

Esterification of pectin substances. II. Pectin acetate and formate. G. SCHNEIDER and M. ZIERVOGEL. III. Molecular size of pectin substances. G. SCHNEIDER and U. FRITSCHI (Ber., 1936, 69, [B], 2530—2536, 2537—2543; cf. B., 1936, 312).—II. Acetylation of pectin depends greatly on pretreatment and is best effected with threads obtained by coagulating its solution in 70% EtOH with 96% EtOH and washing the product with Et_2O . The material is treated with 90—95% of Ac_2O and about 10—5% of AcOH containing H_2SO_4 , $\text{C}_5\text{H}_5\text{N}$, ZnCl_2 , or HClO_4 as catalyst. In consequence of the parallel acetolysis, the product is a degraded, poorly sol. pectin acetate or is little degraded and insol. Treatment of pectin nitrate (I) with Ac_2O in presence of H_2SO_4 , ZnCl_2 , or $\text{C}_5\text{H}_5\text{N}$ at 20° is a homogeneous reaction but complete replacement of NO_2 by Ac appears impossible without degradation. The product is a mixed ester (II) (OAc 30—35%; N 2—3%) sol. in COMe_2 to a viscous solution and with mol. wt. of the same order of magnitude as that of the initial material if the treatment has been cautious. Films obtained from it are somewhat less tenacious than those derived from (I). The affinity of (I) for basic dyes is $>$ that of cellulose nitrate (III), whilst (II) in contrast with cellulose acetate (IV) is strongly dyed; this is not due to admixture with (I). Addition of small amounts of (II) to (III) previous to spinning gives a product with marked affinity for basic dyes. (I) and (II) behave in the same manner as (III) towards acid dyes. Direct formylation of pectin is impossible on account of the degrading action of the acid but mixed esters similar to (II) but of considerably lower mol. wt. are obtained from (I). Treatment of (I) with MeOH containing 1% of HCl at the b.p. and finally at 100° gives a neutral product (OMe 11.6%) very similar to (I). Complete replacement of O- NO_2 by OMe is accompanied by extensive degradation.

III. Osmotic measurements with incompletely dried pectic acid (V) from sterile, dialysed pectin solutions indicate the mol. wt. 30,000—40,000, which must be regarded with caution since it is uncertain whether (V) is unchanged or strongly associated. The mol. wt. of pectin esters (VI), determined osmotically, is very high and varies greatly according to the manner of prep.; (I) obtained by direct nitration of pectin is far more complex than that derived from hydratopectin or (V). The dependence of sp. viscosity of solutions of (VI) on time is similar to that of cellulose esters and the transition of (I) into acetates without alteration in the order of magnitude of the mol. wt. is possible, thus establishing the presence of macro-mols. Fractional pptn. separates (VI) into preps. of varying mol. wt. Röntgenographic and refractive methods show that pectin has thread-like mols. This conclusion is confirmed by the measurement of the viscosity of solutions of polymeric-homologous series of (VI) obtained by variation of time, temp., and concn. during the nitration of pectin, by degradation of the initial products by dil. acid, and by boiling (VI) with H_2O under pressure in analogy with the cellulose esters (VII). The vals. of K_m show that the mols. of (VI) are not so extended as those of (VII), possibly owing to the pres-

ence of the strongly polar CO_2R groups, but more extended than those of starch. H. W.

Methods of determining the constitution of complex natural substances. K. FREUDENBERG (Monatsh., 1936, 69, 144—160).—Tannin, cellulose, starch, condensed tannins, lignin, insulin, and group-sp. compounds are considered. H. W.

Bromination of acetylenic glycols. A. A. KRUGLOV (J. Gen. Chem. Russ., 1936, 6, 925—932).— $(\text{OH}\cdot\text{CPh}_2\cdot\text{C})_2$ and Br in CHCl_3 afford 3:4-dibromo-2:2:5:5-tetraphenyldihydrofuran, m.p. 201°, which with CrO_3 gives COPh_2 and BzOH . $(\text{OH}\cdot\text{CHPh}\cdot\text{C})_2$, m.p. 141°, yields, in addition to $(\text{OH}\cdot\text{CHPh}\cdot\text{CBr})_2$ (I), a small amount of 3:4-dibromo-2:5-diphenyldihydrofuran (?), m.p. 143°. $(\text{OH}\cdot\text{CMe}_2\cdot\text{C})_2$ gives besides $(\text{OH}\cdot\text{CMe}_2\cdot\text{CBr})_2$, 3:4-dibromo-2:2:5:5-tetramethyldihydrofuran, m.p. 49°, b.p. 84—86°/10 mm. (I) and aq. HBr (d 1.65) at 100° give $\text{CHPhBr}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CHPh}\cdot\text{OH}$, m.p. 154°; it is converted by aq. HBr (d 1.76) into a compound, $\text{C}_{16}\text{H}_{12}\text{Br}_4$, m.p. 155°, or by aq. HBr (d 1.66) into a compound, $\text{C}_{16}\text{H}_{12}\text{Br}_4$, m.p. 148°. J. J. B.

Catalytic transformations of heterocyclic compounds. VI. Comparative action of catalysts in the common dehydration of furan and ammonia. J. K. JURIEV and P. M. RATIKIN (Ber., 1936, 69, [B], 2492—2496).—The transformation of furan into pyrrole (I) under the action of NH_3 in presence of Al_2O_3 is a common catalytic dehydration of furan and NH_3 . Good yields are obtained only in the presence of a very energetic dehydrating catalyst (Al_2O_3 at 550°) and at temp. > those required for the common dehydration of EtOH and NH_3 or of EtOH and NH_2Ph . The difference is explained by assuming the necessity of the preliminary rupture of the relatively thermostable furan ring. With less active catalysts (MgSO_4 , active C) and particularly with the dehydrogenating catalyst Fe_2O_3 the yields of (I) are minimal and since traces of (I) are also obtained when a heated empty tube is used it appears that these catalysts behave only as contact substances. Simultaneously fission of furan occurs with loss of O and production of saturated and unsaturated hydrocarbons at the expense of H from NH_3 . The assumption of the intermediate production of δ -amino- α -hydroxy- $\Delta^{\alpha\gamma}$ -butadiene is supported by the formation of CO arising from the tautomeric aldehyde form, $\text{NH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHO}$. H. W.

Synthesis of 3-hydroxychromanone-3-acetic acid. P. PFEIFFER and E. HEINRICH (J. pr. Chem., 1936, [ii], 147, 93—98).—5-Phenoxyethylhydantoin-5-acet-amide, m.p. 232°, and -hydrazide, m.p. 178°, are prepared. α -Phenoxyethylasparagine (A., 1933, 957) and AcCl give the N-Ac derivative, m.p. 222—223° (decomp.), of the anhydride, hydrolysed by EtOH to the N-Ac derivative of the H Et ester. γ -Phenoxy-citramalic acid (diamide, m.p. 183—184°) and AcCl give the anhydride, m.p. 92°, which with warm alkali regenerates the acid, with aq. NH_3 gives the NH_4 salt of the amide, and with AlCl_3 at 115—120° gives 3-hydroxychromanone-3-acetic acid, an oil (Ba salt, cryst.). R. S. C.

Natural coumarins and their action on fish. E. SPÄTH (Monatsh., 1936, 69, 75—114).—A description of the chemistry of natural hydroxy- and methoxy-coumarins and of their nuclear-alkylated derivatives, furocoumarins including those substituted in the furan nucleus, and of β -hydroxycoumarins, with a detailed account of their action on fish. H. W.

Synthesis of 4':5-dihydroxyflavone. I. Z. SYED and T. S. WHEELER (J.C.S., 1936, 1714).—2:6-Dihydroxyacetophenone, *p*-anisic anhydride, and Na *p*-anisate give 5-acetoxy-4'-methoxyflavone, m.p. 171—172°, hydrolysed to the 5-OH-compound, m.p. 155—156°, which with Ac_2O and HI yields 4':5-diacetoxyflavone, m.p. 179—180°, hydrolysed to the 4':5-(OH)₂-compound, m.p. 237—240°. F. R. S.

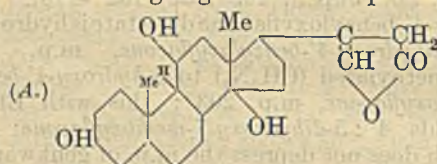
Cuscuta reflexa, Roxb. IV. Isolation of a new yellow flavone colouring matter from the seeds. R. R. AGARWAL (J. Indian Chem. Soc., 1936, 13, 531—536).—The seeds (cf. A., 1936, 1166) yield (in the EtOH extract) 0.1% of a dihydroxytrimethoxyflavone, amarbelin, $\text{C}_{18}\text{H}_{16}\text{O}_7\cdot\text{H}_2\text{O}$, m.p. 234° [Pb and Ag salts; Ac_2 , m.p. 152°, and Bz_2 , m.p. 160° (decomp.), derivatives], demethylated to the hydriodide of amarbelitin, m.p. 204—205° (decomp.), and converted by KOH fusion into protocatechuic acid and a substance, m.p. 168°. E. W. W.

Constituents of Daphne genkwa, Sieb. and Jucc. III. Synthesis of genkwanin. K. TSENG (J. Pharm. Soc. Japan, 1935, 55, 132—145).—5:6-Dihydroxy-4'-benzyloxyflavone diacetate is hydrolysed to 5:7-dihydroxy-4'-benzyloxyflavone, m.p. 305°, which is methylated (CH_2N_2) to 5-hydroxy-4'-benzyloxy-7-methoxyflavone, m.p. 203°; this with EtOH-KOH yields 4':5-dihydroxy-7-methoxyflavone, m.p. 283°, which does not depress the m.p. of genkwanin. CH. ABS. (r)

Biochemistry of Salicaceæ. *Salix daphnoides*.—See A., III, 51.

Vegetable heart poisons. XIII. Constitution of sarmentogenin. R. TSCHESCHE and K. BOHLE (Ber., 1936, 69, [B], 2497—2504).—Treatment of the glucosides from *Strophanthus* seeds in CHCl_3 with Al_2O_3 (Brockmann) leads to cryst. sarmentocymarins, m.p. 160—165° (or $+\text{H}_2\text{O}$, m.p. 136—137°), $[\alpha]_D^{25} -12.2^\circ$ in MeOH, identical with that obtained by Jacobs *et al.* (A., 1929, 729) from *S. sarmentosus*. It is hydrolysed to sarmentogenin (I), m.p. 270°, $[\alpha]_D^{25} +21.3^\circ$ in EtOH, converted by HCl-EtOH into α -anhydrosarmentogenin (II) identical with α -monohydrohispidogenin A (A., 1935, 624) (the latter name should be deleted since the seeds used in its isolation appear to be derived from *S. Barteri*, Franch., and *S. Preussii*, Engl. et Pax, and not from *S. hispidus*). β -Anhydrosarmentogenin-A (*loc. cit.*) appears to have been non-homogeneous. (II) is hydrogenated (PtO_2 in AcOH-EtOAc) to α -tetrahydroanhydrosarmentogenin, m.p. 118—120°, $[\alpha]_D^{25} +11^\circ$ in CHCl_3 (possibly not uniform), converted by cautious oxidation with CrO_3 in AcOH at room temp. into α -tetrahydroanhydrosarmentogenone (III), m.p. 268—270°, $[\alpha]_D^{25} +47.5^\circ$ in CHCl_3 (monoxime, decomp. 240—242°). (III) is oxidised by CrO_3 in AcOH to the dicarboxylic acid (IV), $\text{C}_{23}\text{H}_{32}\text{O}_7$, m.p. 297—

298° (block; decomp.) (Me_2 ester, m.p. 198—199°, $[\alpha]_D^{20} +36.7^\circ$ in $CHCl_3$), which when heated with Ac_2O and then distilled yields the *ketone* (V), $C_{22}H_{30}O_4$, m.p. 222°. Reduction of (III) with $Zn-Hg$ and HCl in $AcOH$ yields the α_1 -monoketone, $C_{23}H_{34}O_3$, m.p. 162°, $[\alpha]_D^{20} +25.5^\circ$ in $CHCl_3$, hydrogenated (PtO_2 in $AcOH$) to the corresponding *alcohol*, $C_{23}H_{36}O_3$, m.p. 226—228. The mother-liquors from (III) contain a second diketone which is reduced (Clemmensen) to the α_2 -monoketone, $C_{23}H_{34}O_3$, m.p. 193°, $[\alpha]_D^{20} +44.6^\circ$ in $CHCl_3$, hydrogenated to the *alcohol*, $C_{23}H_{36}O_3$, m.p. 206—208°, $[\alpha]_D^{20} +49.5^\circ$ in $CHCl_3$, which does not react with molten Bz_2O , with $BzCl$ in C_5H_5N , or with $SOCl_2$ in $CHCl_3$. When distilled with $KHSO_4$ at 170—180°/1 mm. it yields the *dehydrolactone* (VI), $C_{23}H_{34}O_2$, m.p. 174—175°, $[\alpha]_D^{20} +35.5^\circ$ in $CHCl_3$, hydrogenated (PtO_2 in $AcOH$) to the saturated lactone, m.p. 189°, $[\alpha]_D^{20} +35.4^\circ$ in $CHCl_3$, identical with that obtained by Windaus from digitoxigenin. The C skeleton of (I) is therefore identical with that of the other genins of the *Digitalis* group. The presence of the *tert.* OH of (I) at C_{14} has been established by Jacobs. One *sec.* OH is located in ring A [by reason of the formation of (IV) and (V)] and is assumed to be attached to C_{13} as in the other aglucons; it must then be *trans* to Me at C_{10} , since (I) does not give a sparingly sol. compound with digitonin. In sarmentogenone one CO cannot be detected by the usual ketonic reagents and is assumed as in digoxigenone to be present at C_{11} .



The logical consequence that (I) and digoxigenin are stereoisomerides is confirmed by the reduction of tetrahydroanhydrodigoxigenone by Zn and HCl to the *monoketone*, $C_{24}H_{34}O_3$, m.p. 215—218°, $[\alpha]_D^{20} +113^\circ$ in $CHCl_3$, which, when hydrogenated (PtO_2 in $AcOH$) and then distilled with $KHSO_4$, affords (VI). (I) is therefore A.

H. W.

Oxidation-reduction potentials of derivatives of thioindigotin. I. Thioindigotintetrasulphonate. P. W. PREISLER and L. H. HEMPELMANN (J. Amer. Chem. Soc., 1936, 58, 2305—2308).—The oxidation-reduction potentials of the system *K* thioindigotintetrasulphonate (I)—leuco-compound are determined at p_H 0.04—11.18 and 30°; E_0 is 0.409 volt. The reduction involves 2e per mol. of (I) (cf. Remick, A., 1936, 800). (I) is unsuitable as oxidation-reduction indicator except at $p_H < 2.5$. Semiquinone formation occurs at p_H 8.5—11.5. (I) is prepared from thioindigotin and 30% oleum at 145—150° followed by K_2CO_3 .

H. B.

Persulphate oxidation of benzylidenebisthiolacetic acid. B. HOLMBERG (Arkiv Kemi, Min., Geol., 1936, 12, B, No. 2, 4 pp.).—Oxidation of $CHPh(S\cdot CH_2\cdot CO_2H)_2$ (I) in $NaOH$ by either $K_2S_2O_8$ or $I-KI$ affords 5-*keto*-2-phenyl-1:3-*oxithiophan* [2-phenyl-1-oxa-3-thiacyclopentan-5-one] (II), $O=C(CHPh\cdot S\cdot CH_2\cdot CO\cdot CH_2)$ (II),

m.p. 56—58°, relatively stable to alkali and combining with $SH\cdot CH_2\cdot CO_2H$ to give (I). The intermediate stage in the formation of (II) is regarded as $CHPhX\cdot S\cdot CH_2\cdot CO_2Na$ ($X = I$ or $O\cdot SO_3Na$), from which (II) is formed by elimination of NaX (cf. A., 1932, 1235).

J. W. B.

Action of the Grignard reagent on the amide group. X. Synthesis of pyrrolones and pyrroles from *s*-diphenylsuccinic acid. R. LUKEŠ and V. ŠPERLING (Coll. Czech. Chem. Comm., 1936, 8, 461—472; cf. A., 1936, 997).—*meso-s*-Diphenylsuccinic acid and aq. $NH_3\cdot Me$ at 200° give 65% of the *methylimide*, m.p. 110.5°, and 0.5% of *di(methylamide)*, m.p. >300°. The imide and $MgEtBr$ give variable yields of $(CPh\cdot CO)_2NMe$ (I), m.p. 158°, and 3:4-diphenyl-1-methyl-2-ethylpyrrolone (II), m.p. 132°, and a mixture, m.p. (fresh) 188—189°, of stereoisomeric forms of the *hydrate* of (II) [converted into (II) at 180°]. $MgMeI$ gives similarly 3:4-diphenyl-1:2-dimethylpyrrolone, m.p. 108.5°, and its *hydrate*, m.p. 105—115°. $MgPhBr$ gives 2:3:4-triphenyl-1-methylpyrrolone, m.p. 212°, and γ -methylamino- γ -hydroxy- $\alpha\beta\gamma$ -triphenylbutyric acid, m.p. 202—203°. (II) and $MeEtI$ give 3:4-diphenyl-1-methyl-2:5-dichlpyrrole, m.p. 158°, and some (I); $MgPhBr$ gives similarly 3:4:5-triphenyl-1-methyl-2-ethylpyrrole, m.p. 131°.

R. S. C.

Action of Grignard's reagent on ethyl 1-methyl-2-pyrrolone-5-acetate. R. LUKEŠ and J. PREUČIL (Chem. Listy, 1936, 30, 257—260).— Et 1-methyl-2-pyrrolone-5-acetate in C_6H_6 and $MgMeI$ in Et_2O yield *Et* 1:2-dimethylpyrrole-5-acetate, b.p. 135—136°/20 mm., hydrolysed to 1:2-dimethylpyrrole-5-acetic acid, m.p. 119.5° (decomp.). 1-Methyl-2-hexylpyrrole-5-acetic acid, m.p. 89—91° (decomp.) (*Et* ester, b.p. 184—185°/21 mm.), prepared analogously, yields 1:2-dimethyl-5-hexylpyrrole, b.p. 171—172°/71 mm., when heated at the m.p. 2-Phenyl-1-methylpyrrole-5-acetic acid, m.p. 157° (decomp.) (*Et* ester, b.p. 208—210°/18 mm.), and 5-phenyl-1:2-dimethylpyrrole, m.p. 50—51°, are prepared analogously.

R. T.

Action of hydrazine hydrochloride on oximotriphenylpyrrole. III. T. AJELLO and S. GIANFERRARA. IV, V. T. AJELLO (Gazzetta, 1936, 66, 598—608, 608—615, 616—623).—III. The substance $(C_{22}H_{18}ON_3)_2$, m.p. 235—236° (I), obtained in this reaction (A., 1936, 997) is identified as *NN'*-dihydroxy-*NN'*-bis-(4-amino-2:3:5-triphenyl-4-pyrryl)hydrazine. With $NaNO_2\cdot AcOH$ it gives a substance, $(C_{22}H_{16}ON_2)_2$ (II), m.p. 284°, and with $NaOAc\cdot AcOH\cdot NaNO_2$ an isomeride (III), m.p. 206°. Both these give the same *Bz* derivative, m.p. 236°; (III) is converted into (II) by HNO_2 . (I) is oxidised by $KMnO_4\cdot AcOH$ to the *azo-compound*, $(C_{22}H_{16}ON_3)_2$ (IV), m.p. 267° (*Bz* derivative, m.p. 197°), and by $KMnO_4\cdot H_2SO_4$ in $COMe_2$ to the *azoxy-compound* (V), m.p. 233—235°, also obtained from (IV). Both (IV) and (V) are reduced by NH_2OH to aminotriphenylpyrrole.

IV. The product, m.p. 168°, of the original reaction (*loc. cit.*) is identified as triphenylpyrrylhydroxylamine (VI), $N\leq CPh\cdot CH\cdot NH\cdot OH$ (hydrochloride; sulphate; picrate, m.p. 178°; *Bz* derivative, m.p. 175°). This

is readily reduced to aminotriphenylpyrrole. When exposed to light it gives a *product*, $(C_{22}H_{16}N_2)_2O$, m.p. 177°, which with HCl yields an acid substance, $C_{22}H_{17}ON$.

V. The product, m.p. 178°, of the original reaction is also identified as a *triphenylpyrrolylhydroxylamine*, $NH<\begin{smallmatrix} CPh:C-NH\cdot OH \\ CPh:CPh \end{smallmatrix}$ (VII) [*hydrochloride*; *sulphate*; *picrate*, m.p. 193° (decomp.)]. It has stronger reducing properties than (VI), and is converted by acid into a *substance*, $C_{22}H_{17}ON$, m.p. 180–181°, together with (VI). (VII) is reduced to aminotriphenylpyrrole.

E. W. W.

Preparation of triphenylpyrrolylhydroxylamines. T. AJELLO (*Gazzetta*, 1936, 66, 624–630).—Mild acid reducing agents convert oximino-triphenylpyrrole (I) into a mixture of the two triphenylpyrrolylhydroxylamines (II) (cf. preceding abstract); $FeSO_4$, $CuCl$ (which gives an excess of the isomeride of m.p. 168°), or $Zn-(NH_4)_6Mo_7O_{24}$ may be used, in acid solution. Aminotriphenylpyrrole and (I) also yield (II), with a red substance. E. W. W.

Methylation of 3-amino-2-methylindole. New isomeride of *gramine* (*donaxine*). H. ERDTMAN (*Ber.*, 1936, 69, [B], 2482–2485).—Gradual addition of 40% NaOH to a solution of 3-amino-2-methylindole hydrochloride and Me_2SO_4 in MeOH at 25–35° gives 3-dimethylamino-2-methylindole [*picrate*, decomp. 186–187° when rapidly heated; *methiodide*, m.p. 202–205° (decomp.); *methobromide*, m.p. 242–243° (decomp.); *methopicate*, m.p. 204–205°], not identical with *gramine*. 3-Benzamido-2-methylindole has m.p. 233–234°.

H. W.

Manufacture of [hydr]oxylated nitrogen bases.—See B., 1936, 1197.

Metal pyridine complex salts. V. Volume change during formation of cyanates and thiocyanates. T. L. DAVIS and A. V. LOGAN (*J. Amer. Chem. Soc.*, 1936, 58, 2153–2156).—The decreases in mol. vol. which occur when Cu^{II} , Co^{II} , and Ni^{II} cyanates and thiocyanates combine with C_5H_5N to form $M^{II}(NCO)_2 \cdot 6C_5H_5N$ (I) and $M^{II}(NCS)_2 \cdot 4C_5H_5N$ (II) are determined. For (I) the decrease is about 1.74 times that for (II); in both cases the decrease is $Ni > Co > Cu$. The shrinkages are compared with the dissociation pressures. The pressures previously reported (A., 1930, 1522) for $Cu(NCS)_2 \cdot 2C_5H_5N$ are those of $Cu(NCS)_2 \cdot 4C_5H_5N$.

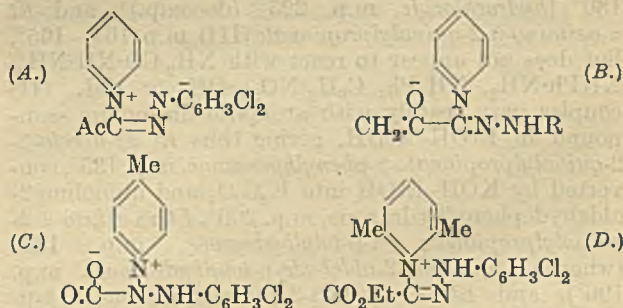
H. B.

Molecular compounds of 1-alkylpyridinium picrates with sodium picrate. F. KROLLFEIFFER and E. BRAUN (*Ber.*, 1936, 69, [B], 2523–2524).—Mol. compounds (1:1) of Na picrate and 1-alkylpyridinium picrates (I) are liable to be formed when (I) are pptd. in presence of Na^+ . The following are described in which $alkyl = Me$, m.p. 210–211°, Et , m.p. 186–187°, Pr^a , m.p. 171–172°, Pr^s , m.p. 195–196°. *n*-Propylpyridinium picrate has m.p. 61–62°. Benzylpyridinium, ethylquinolinium, and ethylisquinolinium, m.p. 179–180°, *picrate* do not give additive compounds.

H. W.

Betaine-like compounds of the pyridine series. P. W. NEBER and H. WÖRNER (*Annalen*, 1936, 526, 173–187).—Bülow's base (I), obtained from 2:4-

dichlorophenylhydrazinopyruvyl chloride (II) and C_5H_5N (A., 1913, i, 999; 1924, i, 674), is converted by H_2SO_4 at 100° into 2:4- $C_6H_3Cl_2 \cdot NH \cdot NH_2$ and C_5H_5N and by $N_2H_4 \cdot H_2O$ in dioxan at 100° into a substance, $C_9H_9ON_3Cl_2$ (II), m.p. 186°, the *Ac* derivative, m.p. 198° (decomp.), of which does not lose H_2O when heated; the probability that (II) is pyruv-2:4-dichlorophenylhydrazidine, m.p. 193° (*loc. cit.*), is diminished by the observation that the latter gives an *Ac* derivative, m.p. 197–198°, which loses H_2O at 200° and forms 3-acetyl-1-2':4'-dichlorophenyl-5-methyl-1:2:4-triazole, m.p. 150°. Boiling NH_2Ph displaces C_5H_5N from (I) with production of 2:4-dichlorophenylhydrazinopyruvanilide, m.p. 129.5°, which is unchanged by short treatment with Ac_2O at 100°, but decomposes when the reaction is prolonged. (II) is slowly transformed by NH_2Ph at 40–50° into a substance, $C_{21}H_{20}ON_4Cl_2$, m.p. 173° (decomp.) (*Ac* derivative, m.p. 181–182°), of unexplained constitution. Phenylhydrazinopyruvyl chloride (III), m.p. 137°, is transformed by C_5H_5N at 60–70° into an analogous base (IV), m.p. 105°, in which C_5H_5N is so loosely retained that it is transformed by boiling EtOH into 5:6-diacetyl-1:4-diphenyl-1:4-dihydro-1:2:4:5-tetrazine, m.p. 168°. The action of HCl in Et₂O on (IV) leads to the hydrochloride of (III). Addition of Cl to (IV) occurs irregularly, whereas Br in $CHCl_3$ yields the compound, $C_{14}H_{12}ON_3Br_3$, decomp. 243° after incipient loss of HBr at 125°. Treatment of (II) with collidine at 40–50° affords a base, $C_{17}H_{17}ON_3Cl_2$, decomp. 158°, very closely analogous to (I), but incapable of formulation according to Bülow's conception of (I); at about 100° the product is $C_{17}H_{15}N_3Cl_2$, vigorous decomp. 180°. It is therefore probable that addition of (I) to C_5H_5N occurs normally at N, and this is followed by loss of HCl to give the betaine A or B. The probability that loss of HCl is a consequence of the tautomerisation of *Ac*, thus leading to B, is supported by the behaviour of Et chloro-2:4-dichlorophenylhydrazinoacetate towards C_5H_5N , whereby the cryst. salt, $C_{15}H_{14}O_2N_3Cl_2 \cdot +1H_2O$, decomp. 142° after incipient darkening at 130°, or $+1EtOH$, decomp. 156°, is produced, which loses Cl and Et (not H) when treated with alkali, thereby giving undoubtedly the betaine C, decomp. 150°; the structure of this is established by its hydro-



lysis with H_2SO_4 to C_5H_5N , 2:4- $C_6H_3Cl_2 \cdot NH \cdot NH_2$, CO, and CO_2 . With collidine, however, HCl is lost and the betaine, $C_{18}H_{19}O_2N_3Cl_2$, m.p. 136° (decomp.), has necessarily the structure D.

H. W.

Pinaflavols. G. B. CRIPPA and T. VERDI (*Annali Chim. Appl.*, 1936, 26, 418–423).—The following have

been prepared and their photographic sensitivity determined: 3-*p*-dimethylaminostyrylpyridine methiodide, m.p. 247°, and ethiodide, m.p. 249°; 6-*p*-dimethylaminostyryl-2-methylpyridine methiodide, m.p. 231°, and ethiodide, m.p. 230°, and 2:6-di-*p*-dimethylaminostyrylpyridine methiodide, m.p. 253°, and ethiodide, m.p. 251° (from 2:6-dimethylpyridine methiodide, m.p. 233°, and ethiodide, m.p. 200°); 2-*p*-dimethylaminostyrylpyridine methiodide and ethiodide. The sensitising action is a function of the alkyl radical attached to the nuclear N, the no. of styryl groups, and their position of attachment to the C_5H_5N nucleus.
L. A. O'N.

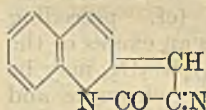
Preparation of derivatives of pyridine and quinoline.—See B., 1936, 1197.

Reaction product of quinoline and ω -chloroacetopyrocatechol. C. MANNICH and W. HOFFMANN (Arch. Pharm., 1936, 274, 472—473).—The structure of 1-3':4'-dihydroxyphenacylquinolinium chloride, m.p. 284° (cf. Mannich *et al.*, A., 1911, i, 565), is correct, whereas quinoline and ω -chloroacetopyrocatechol in EtOH give the salt, m.p. 135° (cf. A., 1894, i, 235).
R. S. C.

Catalytic condensation of acetylene with aromatic amines. III. Condensation of acetylene with aniline in presence of cuprous chloride and nitrobenzene. N. KOZLOV and M. GOLON (J. Gen. Chem. Russ., 1936, 6, 1089—1091).—The yield of tetrahydroquinoline and $NPhEt_2$, formed as by-products in the reaction between C_2H_2 and NH_2Ph (CuCl catalyst), is lowered by introducing $PhNO_2$, which, acting as a H acceptor, prevents hydrogenation of quinoline.
R. T.

Quinolyl-2-pyruvic acid and -2-acetic acid. W. BORSCHKE and R. MANTEUFFEL (Annalen, 1936, 526, 22—46).—Condensation of 2-methylquinoline (I) with $Et_2C_2O_4$ in presence of $KOEt-EtOH-Et_2O$ gives the K derivative of Et 2-quinolylpyruvate (II), transformed by BzCl in boiling Et_2O into Et α -benzoyloxy-2- β -quinolylacrylate, m.p. 114°. (II) and $N_2H_4.H_2O$ in boiling EtOH give partly (I) and $(CO.NH.NH_2)_2$ and partly the hydrazone of 2-quinolylpyruvylhydrazone, m.p. 168—169°. (II) gives Et 2-quinolylpyruvate 2':4'-dinitrophenylhydrazone, m.p. 186° [hydrochloride, m.p. 225° (decomp.)], and Et α -oximino- β -2-quinolylpropionate (III), m.p. 164—165°, but does not appear to react with $NH_2.CO.NH.NH_2$, $NHPh.NH_2$, NH_2Ph , $C_6H_5(NO_2)_3.OH$, or MeI. (II) couples very readily with aromatic diazonium compound in EtOH-AcOH, giving thus Et $\alpha\beta$ -diketo- β -2-quinolylpropionate- β -phenylhydrazone, m.p. 135°, converted by $KOH-EtOH$ into $K_2C_2O_4$ and quinoline-2-aldehydephenylhydrazone, m.p. 206°, Et $\alpha\beta$ -diketo- β -2-quinolylpropionate β -*p*-tolylhydrazone, m.p. 143° (whence quinoline-2-aldehyde-*p*-tolylhydrazone, m.p. 196°), and Et $\alpha\beta$ -diketo- β -2-quinolylpropionate β -*p*-anisylhydrazone, m.p. 150—151° (whence quinoline-2-aldehyde-*p*-anisylhydrazone, m.p. 182°). (II) and aromatic aldehydes in presence of piperidine or $NaOEt-EtOH$ yield aldols and thence saturated lactones, of which α -keto- γ -hydroxy- β -2-quinolyl- γ -phenyl-, m.p. 248° (decomp.), and - γ -*p*-anisyl-, m.p. 255° (decomp.), -butyrolactone are described; (II),

$o-NH_2.C_6H_4.CHO$, and piperidine at 145° give Et 2:3'-diquinolyl-2'-carboxylate, m.p. 140°, hydrolysed to the acid, m.p. 186—187° (decomp.), which is decarboxylated to 2:3'-diquinolyl, m.p. 175°. With $PhCHO$ and $\beta-C_{10}H_7.NH_2$ or $m-C_6H_4.Me.NH_2$ (II) affords 4:5-diketo-2-phenyl-1-2'-naphthyl-, decomp. about 310°, and -1-*m*-tolyl-, m.p. 327—328°, -4-2'-quinolylpyrrolidine. Hydrolysis of (II) by alkali or dil. acid does not proceed satisfactorily, and 2-quinolylpyruvic acid, m.p. 198—199° (decomp.), is best obtained by boiling the K derivative of (II) with technical abs. EtOH. (III) is smoothly hydrolysed by $NaOH-EtOH$ to α -oximino- β -2-quinolylpropionic acid, m.p. 112° (decomp.), which loses CO_2 and H_2O when melted, giving 2-quinolylacetonitrile, m.p. 53—54° (picrate, m.p. 176—177°), and is transformed by Ac_2O into quinolylacetylacetonitrile (IV), m.p. 213—214°.



It is converted by Ac_2O in C_5H_5N into the compound (V) ($R = Me$), decomp. 185—186°, and by $BzCl$ in C_5H_5N into the substance (V) ($R = Ph$), m.p. 172° (decomp.) and, after resolidification, m.p. >260°, converted by HCl into $BzOH$ and (IV). (IV) and the requisite diazonium compound afford 2-quinolylglyoxalonitrile-phenylhydrazone, m.p. 156—158°, and -*p*-bromophenylhydrazone, m.p. 210—212°; the *p*-dimethylaminoanil, m.p. 162°, results from (IV) and $p-NO.C_6H_4.NMe_2$ in MeOH. (IV) and $PhCHO$ in EtOH give α -2-quinolylcinnamonitrile, m.p. 124.5°; 4-methoxy- α -2-quinolylcinnamonitrile, m.p. 148°, and α -2-quinolylcinnamylidenacetone, m.p. 158—160°, are obtained similarly. With $o-OH.C_6H_4.CHO$ in presence of piperidine 3-2'-quinolylcoumarin, m.p. 163.5°, is prepared and isatin gives 2-keto-3-cyano-2'-quinolylmethylene-2:3-dihydroindole, $NH < \begin{smallmatrix} C_6H_4 \\ CO \end{smallmatrix} > C:C(CN).C_9H_6N$, m.p. 268°. cycloHexylidene-2-quinolylacetonitrile, m.p. 118—119°, is obtained in presence of $ZnCl_2$. (IV) and quinoline-2-aldehyde in boiling EtOAc give $\alpha\beta$ -di-2-quinolylacrylonitrile, m.p. 165°. Formyl-2-quinolylacetonitrile, m.p. 231°, obtained from (IV) and boiling HCO_2H or, as Na derivative, from (IV), HCO_2Et , and Na in Et_2O which is then warmed with AcOH, is converted by $NH_2OH.HCl$ in C_5H_5N at 100° into cyano-2-quinolylacetaldoxime, m.p. 252—253° (decomp.), which could not be transformed by Ac_2O into 2-quinolylmalononitrile; it is converted by $NHPh.NH_2$ in $CHCl_3-AcOH$ into cyano-2-quinolylacetaldehydephenylhydrazone, m.p. 195—196°, with a colourless substance, (?) $NPh < \begin{smallmatrix} N=CH \\ C(NH) \end{smallmatrix} > CH.C_9H_6N$, m.p. 234°. 2-Quinolylacetylacetonitrile is obtained from (IV), EtOAc, and $NaOEt$ in Et_2O or from (IV) and Ac_2O . (IV), $Et_2C_2O_4$, and $KOEt$ in Et_2O yield Et cyano-2-quinolylpyruvate, m.p. 191°, and the corresponding acid, m.p. 330—332° (decomp.) after darkening at 315°. Hydrolysis of (IV) by $2N-NaOH$ proceeds smoothly, but the acid decomposes very readily into CO_2 and quinoline-2-aldehyde. With $HCl-EtOH$ (IV) gives Et quinolylacetate, b.p. about 240°/16 mm. (picrate, m.p. 152°; Et_2 quinolylglyoxylatephenylhydrazone, m.p. 107°). α -Hydroxy- β -2-quinolylpropionic acid (VI) (*Me* ester, m.p. 145°), obtained by Einhorn's method,

passes when heated into a substance, $C_{11}H_{11}ON$, m.p. 184°, and 2-quinolylacetaldehyde (VII) [oxime, m.p. 205°, and its *Ac* derivative, m.p. 130°; *semi-carbazone*, m.p. 244° (decomp.)], better obtained by oxidation of the Na salt (VIII) of (VI) with $KMnO_4 \cdot H_2O$ at room temp. Oxidation of (VII) with Ag_2O or, preferably, of (VIII) with $KMnO_4$ yields Einhorn's 2-quinolineacetic acid, m.p. 274—275°, now shown to be *quinoline-3-carboxylic acid* (*picrate*, m.p. 217—218°; *Me* ester, m.p. 76°, and its *picrate*, m.p. 187—188°; *Et* ester, m.p. 65°), which is decarboxylated (Cu-bronze at 250—260°) to quinoline.

H. W.

Synthesis of 6:7-methylenedioxy-1-(3':4'-methylenedioxybenzyl)-3-methylisoquinoline (eupaverine) and 6:7-methylenedioxy-1-phenyl-3-methylisoquinoline. I. KEIMATSU (J. Pharm. Soc. Japan, 1933, 53, 1070—1080).—The above compounds are synthesised by the method of Mannich and Walther (A., 1927, 579). The following are described: 3:4-methylenedioxy-1-(β -nitro- β -methyl- α -methoxyethyl)benzene, b.p. 165—170° (*aurichloride*, decomp. 220°); β -methoxy- β -3:4-methylenedioxyphenyl- α -methyl-ethylamine, b.p. 147—148°/8 mm.; *N*-homopiperonyl- β -methoxy- β -3:4-methylenedioxyphenyl- α -methyl-ethylamine, m.p. 142—144° (*aurichloride*, decomp. 171—173°); *eupaverine aurichloride*, decomp. 202°; *N*-benzoyl- β -methoxy- β -3:4-methylenedioxyphenyl- α -methyl-ethylamine, m.p. 165°; 6:7-methylenedioxy-1-phenyl-3-methylisoquinoline, m.p. 143°; *Et* homopiperonylate, b.p. 145—147°/8 mm.

CH. ABS. (r)

Anti-malarials. I. Anti-malarials from the viewpoint of electronic configuration of their molecules. II. Synthesis of 4-methoxy-2-aminocarbazole and its diethylaminotrimethylene derivatives. A. M. BERKENHEIM (J. Gen. Chem. Russ., 1936, 6, 1039—1042, 1043—1056).—I. The antimalarial action of Plasmocide is ascribed to hydrolysis of the 6-alkoxy- and the 8-dialkylaminomethyleneamino-groups, with production of phenolic OH-groups. Should the β -C of the side-chain have a negative electronic structure ($\cdot NH \cdot C'''$), hydrolysis will result in production of an 8-NH₂-derivative, OH entering into the side-chain. It follows that a prep. with a side-chain of 3 C should be more active therapeutically than with one of 4 C. Similarly hydrolysis of the 6-alkoxy-group takes place more readily in the case of OMe ($C''' \cdot OC'''H_3$) than of OEt ($C''' \cdot OC'''H_2$).

II [with S. I. LURIE]. 4-Chloro-5-nitrobenzoic acid and phenetidine (I) in EtOH (8 hr. at the b.p.) yield 2-nitro-4'-ethoxydiphenylamine-4-carboxylic acid, m.p. 132—136°, the *Me* ester, m.p. 132—136°, of which affords the 2-amino-derivative (II), m.p. 122—125°, when reduced (Zn-AcOH). The *azimine*, m.p. 142—146°, of (II) is converted by heating at 320—340° in paraffin (CO_2 atm.) into 7-carbomethoxy-2-ethoxycarbazole, m.p. 136°. 4-Chloro-3:5-dinitrobenzoic acid (I) or anisidine yield 2:6-dinitro-4'-ethoxy-, m.p. 212—213° (*Me* ester (III), m.p. 158—160°), or 4'-methoxy-diphenylamine-4-carboxylic acid, m.p. 232—234°, from which the corresponding 2:6-(NH₂)₂-derivatives, m.p. 212—214° (*Me* ester, m.p. 111—113°) and 202—204° (IV), respectively, are

obtained by reduction. The *azimine*, m.p. 120—122°, of (III) yields 5-amino-7-carbomethoxy-2-ethoxycarbazole, m.p. 110—115°, when heated at 320—340°, and the *azimine*, m.p. 238—240° (decomp.), of (IV) affords similarly 5-amino-2-methoxycarbazole, m.p. 222—225°. This is condensed with $NEt_2[CH_2]_3Cl$ in EtOH (25 hr.; 100—105°) to give 5-(γ -diethylamino-propyl)amino-2-methoxycarbazole (VI) (*methylene bis-salicylate*). (VI) does not possess plasmocidal activity, although this should, on the basis of the theories proposed in Part I, be present.

R. T.

Chemotherapeutic studies in the acridine series. II. 2-Amino-, 2:5-, 2:7-, and 2:9-diamino-acridines. A. ALBERT and W. H. LINNELL (J.C.S., 1936, 1614—1619).—Condensation of Na 2-chloro-4-nitrobenzoate with the appropriate amine gives 5:4', m.p. 252° (*Ag* salt), and 5:6'-dinitro-, m.p. 239°, and 5-nitro-6'-amino-diphenylamine-2-carboxylic acid, m.p. 207°. Reduction ($SnCl_2$) of these acids yields 3:2'-diaminodiphenylamine dihydrochloride, m.p. 200°, and 3:4'-bisacetamidodiphenylamine, m.p. 186°, whilst ring-closure ($POCl_3$) affords 2:7-, m.p. >350°, and 2:9-dinitroacridone, m.p. 318—320°. With excess of $POCl_3$, 5-nitrodiphenylamine-2-carboxylic acid gives 5-chloro-2-nitroacridone, m.p. 216°, but on distillation of the product, two additive compounds of 2:5-dichloro- and 5-chloro-2-nitroacridine, m.p. 197—200° (1:1) and m.p. 178—181° (2:1), are obtained. Reduction of 2:5-dichloroacridine with $NHPh \cdot NH_2$ yields 2-chloro-5-aminoacridine, m.p. 272—275°, and 2:5-diaminoacridine hydrochloride ($+H_2O$); 2:7-, m.p. 352° (decomp.), and 2:9-diaminoacridone, m.p. >360° are similarly prepared. Further reduction (Na-Hg) gives 2:7-, m.p. 355°, and 2:9-diaminoacridine, m.p. 249°. Proflavine is partly acetylated to 2-amino-8-acetamidoacridine, m.p. 286°. 2-Acetamidoacridine has m.p. 236°.

F. R. S.

2:8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-group in the 5 position. XII. Synthesis of 5-alkylamino-2:8-dimethoxy-10-methylacridinium derivatives. XIII. Synthesis of 5-alkylamino-2:8-dimethoxy-10-ethylacridinium derivatives. XIV. Synthesis of 5-alkylamino-2:8-diethoxy-10-methylacridinium derivatives. K. ISHIHARA (J. Chem. Soc. Japan, 1935, 56, 525—541, 796—810, 952—965).—XII. The 9-*Me*-, -*Et*-, -*Pr*^a-, -*Bu* ^{β} -, and -iso- C_5H_{11} derivatives are described.

XIII. The following derivatives are described. Iodides: 9-*Me*-, m.p. 263°; -*Et*-, m.p. 249—250°; -*Pr*^a-, m.p. 216°; -*Bu* ^{β} -, m.p. 237—238°; -iso- C_5H_{11} -, m.p. 230°. Hydroxides: 9-*Me*-, m.p. 138—140°; -*Et*-, m.p. 126—127°; -*Pr*^a-, m.p. 82—83°; -*Bu* ^{β} -, m.p. 81—82°. Chlorides: 9-*Me*-, m.p. 110°; -*Et*-, m.p. 105°; -*Pr*^a-, m.p. 107°; -*Bu* ^{β} -, m.p. 225—226°. Oxalates: 9-*Me*-, m.p. 146°; -*Et*-, m.p. 173—175°; -*Pr*^a-, m.p. 172—174°; -*Bu* ^{β} -, m.p. 193°.

XIV. The following derivatives are described. Iodides: 9-*Me*-, m.p. 253°; -*Et*-, m.p. 254—256°; -*Pr*^a-, m.p. 259°; -*Bu* ^{β} -, m.p. 140°; -iso- C_5H_{11} -, m.p. 140°. Hydroxides: 9-*Me*-, m.p. 107°; -*Et*-, m.p. 100°; -*Pr*^a-, m.p. 129—130°; -*Bu* ^{β} -, m.p. 126°; -iso- C_5H_{11} -, m.p. 139°. Chlorides: 9-*Me*-, m.p. 242°;

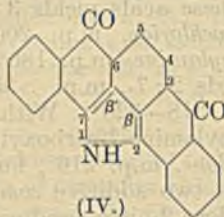
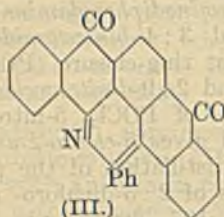
-Et, m.p. 238°; -Pr^a, m.p. 216°; -Bu^β, m.p. 137°; -iso-C₅H₁₁, m.p. 126°. Oxalates: 9-Me, m.p. 180°; -Et, m.p. 140°; -Pr^a, m.p. 115°; -Bu^β, m.p. 190°; -iso-C₅H₁₁, m.p. 135°. CH. ABS. (r)

Preparation of easily soluble salts of dialkylaminoalkylaminoacridines.—See B., 1936, 1179.

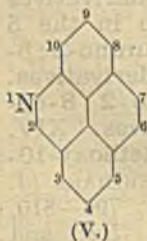
Manufacture of salts of acridinium bases.—See B., 1937, 23.

Preparation of phenanthrolines.—See B., 1936, 1179.

Ring syntheses with *ang*-phthaloylanthraquinones. Dibenzoylene-ββ'-benzopyrrole, phenyldibenzpyrenidinequinone, and triphthaloylbenzene. R. SCHOLL, L. WANKA, and H. DEHNERT (Ber., 1936, 69, [B], 2428—2433).—1-Cyano-2-benzoylanthraquinone, m.p. 263°, accompanied by smaller amounts of anthraquinone-2:1-fluorenone, obtained from 1-amino-2-benzoylanthraquinone



through the diazonium sulphate, is hydrolysed by boiling 75% H₂SO₄ to 2-benzoylanthraquinone-1-carboxylic acid, m.p. 224° after loss of 1 H₂O at about 100°, transformed by conc. H₂SO₄ at 150° or by P₂O₅ and SiO₂ at 140—150° into 1:2-phthaloylanthraquinone (I), m.p. 325°, in small yield. Better results are obtained by heating 1-benzoylanthraquinone-2-carboxylic acid, m.p. 302° [obtained by oxidation of 1-benzoyl-2-methylantraquinone (II) with dil. HNO₃ at 185—190°], with 15% oleum at 100°. (I) is transformed by CH₂Ph·NH₂ in boiling C₅H₅N into 2-phenyl-3:4:9:10-dibenzpyrenidine-5:8-quinone (III), m.p. 272—274°, and 2:3:6:7-dibenzoylene-ββ'-benzopyrrole, (IV), m.p. >385°. The nomenclature of (III) is based on the term "pyrenidine" (from pyrene and pyridine) for the base (V). 1:2:3:4-Dipthaloylanthraquinone, m.p. >400°, is obtained in very small yield when an intimate mixture of 2:3-dichloro-1:4-naphthaquinone and Cu powder is heated at 240°. Chlorination of (II) in C₆H₃Cl₃ at 170° gives 1-benzoyl-2-dichloromethylantraquinone, m.p. 202—202.5°.



H. W.

Syntheses in the pyrazolone series. IV.

Action of aminoguanidines on β-ketonic esters and β-diketones. S. C. DE and P. C. RAKSHIT (J. Indian Chem. Soc., 1936, 13, 509—518).—Aminoguanidine nitrate (I) in H₂O gives with alcoholic CH₂Ac·CO₂Et and its derivatives guanylpiazolones, hydrolysed by boiling aq. KOH. The following are prepared: from CH₂Ac·CO₂Et, 1-guanyl-3-methylpyrazolone nitrate, m.p. 234° (decomp.); from CHMeAc·CO₂Et, 1-guanyl-3:4-dimethylpyrazolone nitrate, m.p. 202° (decomp.); from CHEtAc·CO₂Et,

the 1-guanyl nitrate, m.p. 262° (decomp.), of 3-methyl-4-ethylpyrazolone, m.p. 228°; from CMe₂Ac·CO₂Et, 1-guanyl-3:4:4-trimethylpyrazolone nitrate, m.p. 151° (decomp.); from CHPr^aAc·CO₂Et, 1-guanyl-3-methyl-4-propylpyrazolone nitrate, m.p. 260° (decomp.). CH₂Bz·CO₂Et gives first carbethoxymethylbenzylideneaminoguanidine nitrate, m.p. 200° (decomp.), which when boiled in EtOH yields 1-guanyl-3-phenylpyrazolone nitrate, m.p. 190°. CHBzAc·CO₂Et gives 1-guanyl-4-carbethoxy-5-phenyl-3-methylpyrazolone nitrate, m.p. 222° (decomp.), hydrolysed to 5-phenyl-3-methylpyrazole-4-carboxylic acid, m.p. 262°. CO₂Et·CHAc·CH₂·CO₂Et yields Et 1-guanyl-3-methylpyrazolone-4-acetate nitrate, m.p. 290°, hydrolysed to 3-methylpyrazolone-4-acetic acid. CO₂Et·CH₂·CO·CO₂Et gives Et 1-guanylpiazolone-3-carboxylate nitrate, m.p. 224°. With β-diketones, (I) gives similar products. CHMeAc₂ forms first methylacetylacetonebisaminoguanidine nitrate, m.p. 180° (decomp.), converted on heating into 1-guanyl-3:4:5-trimethylpyrazole nitrate, m.p. 202°. CHEtAc₂, however, gives in the cold 1-guanyl-3:5-dimethyl-4-ethylpyrazole nitrate, m.p. 174°. CH₂BzAc gives first acetonylbenzylideneaminoguanidine nitrate, m.p. 164° (hydrazone), converted into 1-guanyl-3-phenyl-5-methylpyrazole nitrate, m.p. 185°. Similarly CHMeBzAc yields first α-methylacetylbenzylideneaminoguanidine nitrate, m.p. 151°, converted into 1-guanyl-3-phenyl-4:5-dimethylpyrazole nitrate, m.p. 192°. Disubstituted aminoguanidines, NH₂·NH·C(NHR):NR, also react with β-diketones. Thus CH₂Ac₂ yields (R=β-C₁₀H₇) acetylacetonebis(di-β-naphthylaminoguanidine), m.p. 210°, converted by heating in AcOH into 1-di-β-naphthylguanyl-3:4-dimethylpyrazole, m.p. 185°; and (R=p-C₆H₄Me) acetylacetonebis(di-p-tolyl-, m.p. 210°, and (R=Ph) acetylacetonebis(diphenylaminoguanidine), m.p. 225°; the last two do not give pyrazoles. CH₂BzAc yields (R=Ph) benzoylacetonebis(diphenyl-, m.p. 115°, and (R=p-C₆H₄Me) benzoylacetonebis(di-p-tolylaminoguanidine), m.p. 146°, converted on heating in AcOH into 1-diphenyl-, m.p. 230°, and 1-di-p-tolyl-guanyl-3-phenyl-4-methylpyrazole, m.p. 220°, respectively. The following are obtained from β-ketonic esters: CH₂Ac·CO₂Et yields (R=β-C₁₀H₇) carbethoxyisopropylideneamino-di-β-naphthyl-, m.p. 141°, (R=p-C₆H₄Me) -di-p-tolyl-, m.p. 258°, and (R=Ph) -diphenyl-guanidine, m.p. 242°, converted respectively into 1-di-β-naphthyl-, m.p. 290°, 1-di-p-tolyl-, m.p. 210°, and 1-diphenyl-guanyl-3-methylpyrazolone, m.p. 198°. Similarly CH₂Bz·CO₂Et furnishes carbethoxymethylbenzylideneamino-di-β-naphthyl-, m.p. 219°, -di-p-tolyl-, m.p. 225°, and -diphenyl-guanidine, m.p. 232°, converted into 1-di-β-naphthyl-, m.p. 180°, 1-di-p-tolyl-, m.p. 249°, and 1-diphenyl-guanyl-3-phenylpyrazolone, m.p. 206°.

E. W. W.

Barbituric acid derivatives. I. Synthesis of 4-imino-5-methylthiolbarbituric acid. Preparation of [methyl] α-cyanopropionate. T. NISHIKAWA (J. Chem. Soc. Japan, 1935, 56, 936—945).

CH. ABS. (r)

4-N-Phenylpiperazinesulphonic acid. V. PRELOG (Arh. Hemiju, 1936, 10, 49—51).—1-Phenylpiperazine with conc. H₂SO₄ at 180—190° gives

1-phenylpiperazine-p-sulphonic acid (Na salt; hydrochloride; Bz derivative). F. R.

Phenazine series. IV. Octa- and per-hydrophenazines. G. R. CLEMO and H. MCILWAIN (J.C.S., 1936, 1698—1701).—Attempts to resolve the two isomeric 1:2:3:4:9:10:11:12-octahydrophenazines (d-tartrate, m.p. 222°) have been unsuccessful. α -, β -, and γ -Perhydrophenazines have been prepared by reduction of the H_8 -compounds under different conditions, and their interconversion studied. The configurations of the compounds have been established by an examination of their physical properties, and of the reactions which lead to their formation. F. R. S.

Manufacture of free ω -methanesulphonic acids of pyrazoloneamines.—See B., 1936, 1144.

Manufacture of salts of cyclic nitrogenous bases.—See B., 1936, 1179.

Reaction of certain diazosulphonates derived from β -naphthol-1-sulphonic acid. XVI. Constitution and reactions of 1-methoxy-3-(4'- and 3'-nitroaryl)-4-methylene-3:4-dihydrophthalazines. F. M. ROWE and H. J. TWITCHETT (J.C.S., 1936, 1704—1713).—The O of the 1-keto-group of 4'- and 3'-nitro-3-aryl-4-methylphthalaz-1-ones is best methylated with Me_2SO_4 alone at 50—70°. Addition of Na_2CO_3 to an aq. solution of the methosulphate produces an orange-yellow gelatinous ppt. which coagulates rapidly with the elimination of H_2O and formation of the red pseudo-base

$C_6H_4 \begin{smallmatrix} \diagup C(OMe):N \\ \diagdown C(CH_3):NR \end{smallmatrix}$ (I). The constitution of (I) has been confirmed by reactions characteristic of compounds containing an external $:CH_2$. Compounds of type (I) crystallise readily and can be preserved without decomp. but show low basicity and reactivity. The following have been prepared: 1-methoxy-3-(4'-nitrophenyl)-, m.p. 199° (decomp.), -(3'-nitrophenyl)-, m.p. 223—224°, and -(2':6'-dichloro-4'-nitrophenyl)-4-methylphthalazinium, m.p. 228°, and 1-methoxy-3-(4'-nitrophenyl)-, m.p. 249°, and -(3'-nitrophenyl)phthalazinium perchlorate, m.p. 215°. HNO_3 or $p-NO-C_6H_4-NMe_2$ with 1-methoxy-3-(4'-nitrophenyl)-4-methylene-3:4-dihydrophthalazine (II) gives the corresponding 4-keto-compound. (II) and CH_2PhI afford 1-methoxy-3-(4'-nitrophenyl)-4-(β -phenylethyl)phthalazinium iodide, m.p. 185° (3'- NO_2 -isomeride, m.p. 174°). (II) condenses with 2-oximinomethyl-3:3-dimethylindolenine methoperchlorate to form (1:3:3-trimethyl-2-indolenino)(1'-methoxy-3'-p-nitrophenyl-3':4'-dihydro-4'-phthalazino)-cyanine perchlorate, m.p. 182°. The perchlorates of (I) with $p-CHO \cdot C_6H_4 \cdot NMe_2$ in Ac_2O give 1-methoxy-3-(4'-nitrophenyl)-, m.p. 238°, -(2':6'-dichloro-4'-nitrophenyl)-, m.p. 254° (decomp.), and -(3'-nitrophenyl)-4-p-dimethylaminostyrylphthalazinium perchlorate, m.p. 198°. (II) and its perchlorate with Et orthoformate or diphenylformamidine yield bis-(1-methoxy-3-p-nitrophenyl-3:4-dihydro-4'-phthalazino)carbocyanine perchlorate, m.p. 258—260° (decomp.) [m- NO_2 -isomeride, m.p. 244° (decomp.)]. Diphenylformamidine and 1:2:3:3-tetramethylindolenine perchlorate in Ac_2O afford 1:3:3-trimethyl-2- β -acetanilidovinyl-

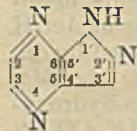
indoleninium perchlorate (III), m.p. 245°, hydrolysed to the -2- β -anilino-compound, m.p. 253°. (III) and (I) in Ac_2O give (1:3:3-trimethyl-2-indolenino)(1'-methoxy-3'-[4'-nitrophenyl]-3':4'-dihydro-4'-phthalazino)carbocyanine perchlorate, m.p. 265° (decomp.) [(2':6'-dichloro-4'-nitro)-isomeride, m.p. 246°]. 5-Chloro-2- β -acetanilidovinylbenzthiazole ethiodide and 1-methoxy-3-(2':6'-dichloro-4'-nitrophenyl)-4-methylene-3:4-dihydrophthalazine in Ac_2O lead to (5-chloro-2-ethyl-1-benzthiazolo)(1'-methoxy-3'-[2':6'-dichloro-4'-nitrophenyl]-3':4'-dihydro-4'-phthalazino)-carbocyanine iodide, m.p. 254°. (II) and 1-phenyl-3-methyl-4-anilinomethylene-5-pyrazolone in $AcOH$ give 1-methoxy-3-p-nitrophenyl-4-(5'-keto-1'-phenyl-3'-methylpyrazolinylidene-ethylidene)-3:4-dihydrophthalazine, m.p. 258°. Compounds of type (I) react with diazo-compounds to form 1-methoxy-3-(4'-nitrophenyl)-4-(benzeneazomethyl)-, m.p. 224°, and -(4'-nitrobenzeneazomethyl)-phthalazinium perchlorate, m.p. 268°, and its (3'- NO_2)-, m.p. 235°, and (2':6'-dichloro-4'-nitrophenyl) isomerides, m.p. 254°. (I) and 2:4-dinitrochlorobenzene yield 1-methoxy-3-(4'-nitrophenyl)-4-(2':4'-dinitrobenzylidene)-3:4-dihydrophthalazine, m.p. 255° (3'- NO_2 -isomeride, m.p. 210°). 2-(2':4'-Dinitrobenzylidene)-1:3:3-trimethylindolinc, m.p. 137°, 2-(2':4'-dinitrobenzylidene)-1-ethyl-1:2-dihydroquinoline, m.p. 180°, and 1-phenyl-4-(2':4'-dinitrophenyl)-3-methyl-5-pyrazolone, m.p. 215°, are similarly prepared. None of the derivatives of (I) possesses any marked sensitising properties, but some are good desensitisers. F. R. S.

Basic constituents in secretions of various species of toads.—See A., III, 9.

Production of cyclical disubstituted [1:5-poly-methylene]tetrazoles.—See B., 1936, 1198.

Pyrazopyrazines. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1936, 66, 649—652).—5-Amino-4-benzeneazopyrazoles condense with $CH_2R \cdot CO \cdot R'$ at 210° to give derivatives of pyrazopyrazine [pyrazolo-4':5'-5:6-pyrazine] (A). Thus 5-amino-4-benzeneazo-1-phenyl-3-methylpyrazole (I) gives, with $COPhMe$, 1':2-diphenyl-3'-methyl-, m.p. 186°, with $COPhEt$, 1':2-diphenyl-3:3'-dimethyl-, m.p. 170°, and, with $p-C_6H_4MeAc$, 1'-phenyl-2-p-tolyl-3'-methylpyrazolo-4':5'-5:6-pyrazine, m.p. 192°. With $o-C_6H_4(CO)_2O$, (I) yields the corresponding 3-phthalimido-derivative, m.p. 184°.

Murexide question. D. DAVIDSON and E. ERSTEIN (J. Org. Chem., 1936, 1, 305—314).—The evidence in favour of the usual formulæ for murexide (I) and alloxantin (II) is discussed and accepted. Contrary to statements in the lit., uramil (III) is readily hydrolysed by hot HCl, the reaction being accelerated by alloxan (IV) or $FeCl_3$, but retarded by Sn; reaction probably occurs by oxidation-reduction of (II) and (IV) to dialuric acid (V) and alloxanimine (VI), (VI) then yielding NH_3 and regenerating (IV). (V) is also hydrolysed by hot HCl, giving tartronic acid. The formation of (I) from (II) and NH_4 salts probably occurs thus: (II) \rightarrow (IV) + (V); (V) + $NH_4X \rightarrow$ (III); (III) + (IV) \rightarrow purpuric acid \rightarrow (I).



(A.)

A similar mechanism, $(IV) + NH_3 \rightarrow (VI)$; $(VI) + (V) \rightarrow (III)$; $(III) + (IV)$ or $(VI) \rightarrow$ purpuric acid, is proposed. Other methods of obtaining (I) are similarly explained. R. S. C.

Preparation of *p*-diethylaminobenzaldehyde. M. Q. DOJA and A. MOKBET (J. Indian Chem. Soc., 1936, 13, 542—543).—Methods of preparing alloxantin and alloxan from uric acid, and alloxandiethylanil, are described. *p*- $NEt_2 \cdot C_6H_4 \cdot CHO$ could not be obtained by the method of Boehringer (B., 1900, 557), nor by hydrolysis of *pp'*- $NEt_2 \cdot C_6H_4 \cdot CH \cdot N \cdot C_6H_4 \cdot NMe_2$ or of *p'*-diethylamino-benzylidene-*p*-aminodiethylaniline, m.p. 147—149° (from $NPhEt_2$, CH_2O , HCl , and *p*- $NO \cdot C_6H_4 \cdot NEt_2$). E. W. W.

Absorption of light and tautomerism of uric acid. H. FROMHERZ and A. HARTMANN (Ber., 1936, 69, [B], 2420—2428; cf. A., 1936, 1317).—Measurements of light absorption show that uric acid (I) and its salts invariably exist in the keto-form even in alkaline solution. Its acidic nature cannot therefore depend on a complete or partial enolisation and dissociation of H from O; as a consequence of the vicinity of unsaturated groups H dissociates directly from N. Traces of a OH-form in (I) must be assumed to explain the interaction of (I) and CH_2N_2 . H. W.

Oxidation product of urobilin. L. HEHMAYER and P. BEICKERT (Z. physiol. Chem., 1936, 244, 99—101).—Urobilin hydrochloride on oxidation with H_2O_2 or $KClO_3$ gives a very labile pigment, exhibiting max. absorption at 520 mμ. It is stable in acid, but loses its colour on exposure to air and light and in neutral and alkaline solutions. W. McC.

Porphyrins. XXXIX. Formylpyrroporphyrin and formyldeuteroporphyrin. H. FISCHER and L. BEER (Z. physiol. Chem., 1936, 244, 31—55; cf. A., 1936, 1270).—The yield of formylpyrroporphyrin (I) from pyrrohaemin is increased to 50% by using $SnBr_4$ as catalyst at 50—55°. The Me_2 ester of the condensation product (II) of (I) with $CH_2(CO_2H)_2$ after elimination of CO_2 yields mesoporphyrin-IX with $Pd-H_2$. (II) with HBr in $AcOH$ gives an additive compound which, hydrolysed by dil. aq. $NaOH$ and treated with CH_2N_2 , gives the Me_2 ester (III), m.p. 224°, of pyrroporphyrin-6-β-hydroxypropionic acid. (II) combines with $CHN_2 \cdot CO_2Et$, and the product on treatment with CH_2N_2 gives the compound, $C_{39}H_{44}N_6O_6$, m.p. 265°, which contains a pyrazoline ring. Conc. H_2SO_4 reconverts (III) into (II) and CrO_3 in $AcOH$ converts it into the corresponding keto-acid. The Me ester of (I) in $CHCl_3$ combines with HCN to give a hydroxynitrile, m.p. 232°, and with NH_4CN to give a substance, m.p. 238°. (I) with $MgMeI$ gives 6-hydroxyethylpyrroporphyrin, which at 205° in a high vac. yields a product converted by CH_2N_2 into the Me ester, m.p. 221°, of 6-vinylpyrroporphyrin (IV). The Me ester of (IV) with $CHN_2 \cdot CO_2Et$ gives a substance, m.p. 230°. (IV) reduced with HI in $AcOH$ gives the corresponding monocarboxylic acid, m.p. 270°. (I) with $MgEtI$ gives 6-hydroxypropylpyrroporphyrin, from which H_2O is eliminated at 205° in a high vac., with allyl Mg iodide a substance, m.p. 290° and with $MgPhI$

hydroxybenzylpyrroporphyrin. The Fe salt of the Me ester of (I) oxidised by air- $HI-AcOH$ and then esterified with CH_2N_2 gives the Me ester of the corresponding rhodoporphyrin (V) with conversion of CHO into CO_2H . The oxime of the Me ester of (I) boiled with Ac_2O and $NaOAc$ loses H_2O and gives the Me ester, m.p. 239° (Fe salt, m.p. 312°), of 6-cyanopyrroporphyrin, which resists acid and alkaline hydrolysis, but is converted by 30% KOH in $MeOH$ at 145° into (V). The Me ester of (I) with $MeNO_2$ in presence of $NHET_2$ yields, after esterification with CH_2N_2 , the Me ester, m.p. 228°, of 6-(ω-nitrovinyl)-pyrroporphyrin, with $AcCO_2H$ in boiling Ac_2O in presence of $NaOAc$, with $CH_2(CN)_2$, or with $CH_2(CO_2Et)_2$ a substance, m.p. 274°, and reacts with $CN \cdot CH_2 \cdot CO_2Et$, and with $NH_3 \cdot Me \cdot HCl$. Deuterohaemin with $POCl_3$ and $CHCl_2 \cdot OEt$ gives the Me ester (VI), m.p. 232° [Cu salt, m.p. 212°; oxime (VII), m.p. 226°], of formyldeuteroporphyrin (VIII) and (VI) with $CH_2(CO_2H)_2$ in presence of piperidine gives the Me ester (IX), m.p. 195° (Fe salt, m.p. 263°; Cu salt, m.p. 216°), of the corresponding deuterocacrylic acid. (VI) with $CH_2(CO_2Me)_2$ gives the Me_2 ester, m.p. 206°. (IX) with $CHN_2 \cdot CO_2Et$ followed by esterification with CH_2N_2 gives a substance, m.p. 220°, containing a pyrazoline ring and with boiling Ac_2O and $NaOAc$ followed by esterification with CH_2N_2 the Me_2 ester, m.p. 207° (Fe salt, m.p. >320°), of 4-cyanodeuteroporphyrin. (VII) boiled in $AcOH$ with HI in a current of air gives the Me_2 ester of 4-carbomethoxy-1 : 3 : 5 : 8-tetramethylporphin-6 : 7-dipropionic acid. (VIII) with $MgMeI$ gives a product which with CH_2N_2 yields the Me ester, m.p. 206°, of hydroxyethyldeuteroporphyrin, and this ester in a high vac. at 115° gives 4-vinyldeuteroporphyrin. Together with (VIII) diformyldeuteroporphyrin (X) (dioxime) is produced. (X) with $CH_2(CO_2H)_2$ gives the corresponding diacrylic acid, which combines with $CHN_2 \cdot CO_2Et$ and with HI in a current of air giving the corresponding tetracarboxylic acid. W. McC.

Ultra-violet spectrum of hæmoglobin and its derivatives.—See A., I, 8.

Compound isolated from scallop mussel.—See A., III, 8.

Synthesis of morpholine. B. L. HAMPTON and C. B. POLLARD (J. Amer. Chem. Soc., 1936, 58, 2338—2339; cf. Knorr, A., 1889, 1218).— $NH(CH_2 \cdot CH_2 \cdot OH)_3$ is mixed with conc. HCl until acid to litmus, H_2O is evaporated, and the residue is heated at 200—210°/15 hr.; subsequent distillation with CaO gives 48% of morpholine (*N*-2-chlorocinchoninyl derivative), whilst steam distillation of the alkaline ($NaOH$) mixture and absorption in HCl affords 65% of the hydrochloride. H. B.

Manufacture of ether derivatives of morpholine alcohols.—See B., 1936, 1198.

Condensation of picryl chloride with 4-methylthiazole and benzthiazole. (MISS) M. L. TOMLINSON (J.C.S., 1936, 1607—1609).—4-Methylthiazole and picryl chloride (I) give 2-hydroxy-3-picryl-4-methyl-2 : 3-dihydrothiazole (II), m.p. 181° (decomp.) [picrate, m.p. 194° (decomp.)], whilst benzthiazole with (I) yields 1-hydroxy-2-picryl-1 : 2-dihydrobenz-

thiazole (III), m.p. 180° (decomp.), which with Na_2CO_3 affords 2:4-dinitro-5-formylphenanthiazine, m.p. 243° (decomp.). 2:2'-Bisformamidodiphenyl disulphide, m.p. 161°, and (I) in presence of Cu condense to (III). (II) and (III) dissolve slowly in alkali with ring-opening. F. R. S.

Preparation of aminobenzthiazole compounds.
—See B., 1936, 1235.

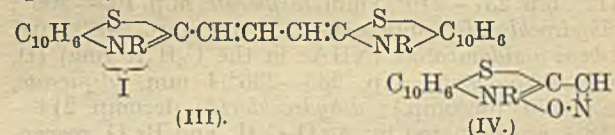
Unsaturated and tautomeric mobility of heterocyclic compounds. VIII. β -Naphthathiazole, 5:6:7:8-tetrahydro- β -naphthathiazole, and 5-phenylbenzthiazole derivatives. R. D. DESAI, R. F. HUNTER, and M. A. KUREISHY. IX. Methylation of 5-substituted 1-thiolbenzthiazoles, and the ultra-violet absorption of mobile and static derivatives of 1-thiolbenzthiazole. C. HASAN and R. F. HUNTER (J.C.S., 1936, 1668—1671, 1671—1675).—VIII. α -Naphthylthiocarbamide with Br (1 mol.) gives 2-amino- β -naphthathiazole (I), m.p. 190° (Ac derivative, m.p. 280°), but with excess of Br yields the 4-Br-derivative, m.p. 243°, also derived from 4-bromo- α -naphthylthiocarbamide, m.p. 108°, and Br. Methylation (MeI) of (I) affords 2-acetimido-1-methyl-1:2-dihydro- β -naphthathiazole, m.p. 180°. 2-Acetmethylamido- β -naphthathiazole, m.p. 160°, is obtained by acetylation of the corresponding NHMe compound. 2-Chloro- β -naphthathiazole, m.p. 82°, obtained from α -naphthylthiocarbimide and PCl_5 , with NH_2Ph yields 2-anilino- β -naphthathiazole, m.p. 142° (picrate, m.p. 193°), methylated to 2-anilino-1-methyl-1:2-dihydro- β -naphthathiazole picrate, m.p. 204°, and 2-methylanilino- β -naphthathiazole, m.p. 111—112° (picrate, m.p. 156°). α -Naphthylthiourethane is oxidised [$\text{K}_3\text{Fe}(\text{CN})_6$] to 2-ethoxy- β -naphthathiazole, m.p. 50°, hydrolysed to the 2-OH-compound, m.p. 300°, which is methylated (Me_2SO_4) to 2-keto-1-methyl-1:2-dihydro- β -naphthathiazole, m.p. 153°. Me α -naphthylthioncarbamate, m.p. 95°, is oxidised [$\text{K}_3\text{Fe}(\text{CN})_6$] to 2-methoxy- β -naphthathiazole, m.p. 62°, also obtained from the Cl-compound. ar-Tetrahydro- α -naphthylthiocarbimide, m.p. 34°, is obtained from the corresponding amine and CSCl_2 ; ar-tetrahydro- α -naphthylthiocarbamide, m.p. 161°, and Br give 2-amino-5:6:7:8-tetrahydro- β -naphthathiazole, m.p. 174°, which is methylated to 2-acetimido-1-methyl-1:2:5:6:7:8-hexahydro- β -naphthathiazole, m.p. 171°. s-ar-Tetrahydro- α -naphthylmethylthiocarbamide, m.p. 158°, 2-methylamino-5:6:7:8-tetrahydro- β -naphthathiazole, m.p. 169° (Ac derivative, m.p. 158°), p-xenylthiocarbimide, m.p. 119—120°, and thiocarbamide, m.p. 204°, 1-amino-5-phenylbenzthiazole, m.p. 226—227°, methylated to 1-imino-5-phenyl-2-methyl-1:2-dihydrobenzthiazole, m.p. 165°, s-p-xenylmethylthiocarbamide, m.p. 170°, and 1-methylamino-5-phenylbenzthiazole, m.p. 203°, are also described. Alkylation shows that 2-amino- β -naphthathiazole reacts apparently exclusively in the amino-aromatic form, but substitution of a H of the NH_2 by Ph causes appreciable reactivity in the iminodihydro-form.

IX. 1-Thiol-5-methylbenzthiazole is methylated (Me_2SO_4) to 1-methylthiol-5-methylbenzthiazole, m.p. 48°, unaccompanied by any detectable amount of 1-thio-2:5-dimethyl-1:2-dihydrobenzthiazole, m.p.

138°, obtained from the 1-nitrosoimino-compound and P_2S_5 . 5-Bromo-1-thiolbenzthiazole, m.p. 272°, is methylated to (mainly) 5-bromo-1-methylbenzthiazole, m.p. 102°, and 5-bromo-1-thio-2-methyl-1:2-dihydrobenzthiazole, m.p. 135°. 5-Nitro-1-thiol is methylated to 5-nitro-1-methylthiol-benzthiazole, m.p. 126°. The absorption spectrum of 1-thiol-5-methylbenzthiazole indicates that it must possess the thiodihydro-structure. F. R. S.

Aneurin. III. Synthesis of thiochrome and related compounds. A. R. TODD, F. BERGEL, H. L. FRAENKEL-CONRAT, and (Miss) A. JACOB (J.C.S., 1936, 1601—1605).—Et 4-hydroxy-2-methylpyrimidine-5-acetate, m.p. 178°, prepared from acetamidine hydrochloride and Et formylsuccinate, with N_2H_4 gives 4-hydroxy-2-methylpyrimidine-5-acetylhydrazide, m.p. 246°. The hydrazide with $\text{C}_5\text{H}_{11}\text{O}\cdot\text{NO}$ affords 4-hydroxy-5-urethanomethyl-2-methylpyrimidine, m.p. 173°, hydrolysed to the 5- $\text{NH}_2\cdot\text{CH}_2$ compound (hydrochloride, m.p. 278—282°; thioformyl, m.p. 199—200°, and Ac derivatives, m.p. 219—220°), which is converted into the 5-OH- CH_2 compound, m.p. 215—216°. The OH-compound with POCl_3 yields 4-chloro-5-chloromethyl-2-methylpyrimidine, m.p. 54°, which with 2-amino-4-methyl-5- β -hydroxyethylthiazole (I) (picrate, m.p. 213°) gives thiochrome, identical with the product obtained from aneurin. 2:4-Dichloro-5-chloromethyl-6-methylpyrimidine, m.p. 38—39°, obtained from the OH-compound, with 2-amino-4-methylthiazole gives 9-chloro-3:7-dimethylthiochromine, m.p. 291—292° (decomp.), and with (I) yields 9-chloro-3:7-dimethyl-2- β -hydroxyethylthiochromine, m.p. 260—261° (decomp.). F. R. S.

Thiazines. III. Synthesis of cyanine dyes of the perinaphtho-m-thiazine series. H. VAN B. JOY and M. T. BOGERT (J. Org. Chem., 1936, 1, 236—244; cf. A., 1932, 176).—The prep. of 1:8- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_2\text{Cl}$ and 2-methylperinaphtho-m-thiazine (I) is modified. The methiodide (II), m.p. about 222—230° (decomp.), of (I) with $\text{CH}(\text{OEt})_3$ in $\text{C}_5\text{H}_5\text{N}$ gives the carbocyanine (III; $\text{R}=\text{Me}$), + CHCl_3 , decomp. 222°, and with p-NMe $_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in EtOH or Ac_2O gives 2-p-dimethylaminostyrylperinaphtho-m-thiazine methiodide, m.p. 235° (decomp.); the corresponding hydriodide, m.p. 243° (decomp.), is similarly



obtained from the hydriodide (impure), decomp. 259°, of (I). (I) and EtI give a mixture of hydriodide and ethiodide, which with $\text{CH}(\text{OEt})_3$ and $\text{KOAc}\cdot\text{Ac}_2\text{O}$ (not $\text{C}_5\text{H}_5\text{N}$) gives the dye (III; $\text{R}=\text{Et}$), + CHCl_3 , decomp. 243°. (II), $\text{NHPh}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{NPh}$, and KOAc in Ac_2O give an impure dicarbocyanine, m.p. 221° (decomp.). The methochloride, decomp. 234—235°, or hydrochloride, decomp. 233—234°, of (I) with $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_{11}\text{O}\cdot\text{NO}$ give a (?) furazan derivative (IV; $\text{R}=\text{Me}$), $\text{C}_{13}\text{H}_{10}\text{ON}_2\text{S}$, decomp. 236°, or (IV; $\text{R}=\text{H}$), decomp. 237—238°, respectively. The dyes have single absorption max. and little sensitising power. R. S. C.

Dicarbocyanines with substituents in the chromophore. Z. P. SITNIK and B. S. STEINGARDT (J. Appl. Chem. Russ., 1936, 9, 1842—1851; cf. Kiprianov *et al.*, A., 1936, 1002).—The 1:1'-diethyl-, m.p. 230°, 1:1'-diethyl-6:7:6':7'-dibenzo-, m.p. 210°, 10-bromo-1:1'-diethyl-, m.p. 171—172°, 10-methyl-1:1'-diethyl- (I), m.p. 250°, 5:5':10-trimethyl-1:1'-diethyl- (II), m.p. 254°, 10-methyl-1:1'-diethyl-6:7:6':7'-dibenzo-, m.p. 210—211°, and 8:12-dimethyl-1:1'-diethyl-thiodicarbocyanine iodide (III) (N=1; S=3) were prepared from the appropriate substituted benzthiazole and the corresponding acraldehyde acetals. (I), (II), and (III) sensitise photographic emulsions. The acetal $\text{HBr}\cdot\text{NHPH}\cdot\text{CH}:\text{CMe}\cdot\text{CH}(\text{OMe})_2$, m.p. 234°, was prepared from $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CH}(\text{OMe})_2$, b.p. 135—138°/40 mm. J. J. B.

Tobacco bases. VIII. New tobacco alkaloids. Rhœadine, *l*-peganine, and ammoresinol. E. SPATH and E. ZALIC (Ber., 1936, 69, [B], 2448—2452; cf. A., 1935, 1387).—The most volatile fractions of the subsidiary alkaloids of nicotine are converted into their hydrochlorides, and these are extracted with CHCl_3 , which leaves much undissolved NH_4Cl . The *sec.* and *tert.* bases are separated from one another by means of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, whereby piperidine among other *sec.* amines is identified. NMe_3 is also present. Fractional extraction with acid of the portion of b.p. 120—140°/1 mm. leads to the isolation of 2:3'-dipyridyl. Rhœadine (A., 1936, 1003) does not evolve CH_4 (Zerevitinov) at 18° or 85°, whereas rhœagenine contains 1 active H. Contrary to Rosenfeld *et al.* (A., 1936, 1394), the authors have never attempted to isolate *l*-peganine from *Peganum Harmala*, L.; its prep. from this source by Rosenfeld supports the authors' view that it is optically active in the plant, but is readily racemised during isolation therefrom. Reply is made to Raudnitz *et al.* (A., 1936, 1259) with regard to ammoresinol. H. W.

1- and 5-Amino- and -acylamino-nicotines. J. L. GOLDFARB (Arch. Pharm., 1936, 274, 490—497).—5-, m.p. 106—107°, b.p. 183°/2 mm. (*dipicrate*, m.p. 185—186·5°; *hydrochloride*), and 1-*acet*-, b.p. 169—170°/3·5 mm., m.p. 35—37° (*dipicrate*, m.p. 183·5—184·5°; *hydrochloride*), and 5-, m.p. 110·5—112°, b.p. 237—240°/5 mm. (*dipicrate*, m.p. 199—200°; *dihydrochloride*, sinters at 225°, decomp. 240°), and 1-benz-amidonicotine (NHAc in the $\text{C}_5\text{H}_5\text{N}$ ring) (I), m.p. 98·5—99·5°, b.p. 235—236°/4 mm. [*dipicrate*, m.p. 230° (decomp.)]; *dihydrochloride*, decomp. 214—218°], are prepared by $\text{Ac}_2\text{O}\cdot\text{C}_6\text{H}_6$ and Bz_2O , respectively. Less cautious acetylation gives only resins. (I) dissolves in aq. NaOBz and is pptd. therefrom by addition of H_2O as *hydrate*, $+\text{H}_2\text{O}$, m.p. 76°. Striking differences in the physiological properties of nicotine and its NH_2 - and acylamino-derivatives are recorded. R. S. C.

Synthesis and constitution of gramine. T. WIELAND and C. Y. HSING (Annalen, 1936, 526, 188—194).—Interaction of Mg 5-methoxy-3-indolyl iodide with $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CN}$ gives 5-methoxy-3-dimethylaminomethylindole, m.p. 128° (*picrate*, m.p. 168°; *methiodide*, m.p. >280°), CN behaving as a halogen in the reaction and being eliminated as

MgICN . Similarly, Mg 3-indolyl iodide and $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CN}$ give 3-dimethylaminomethylindole (I). The base, its picrate, platinichloride, and perchlorate appear identical with natural gramine (donaxine) and its salts, but its methiodide has m.p. >280°, whereas that derived from gramine has m.p. 175—176°. (I) gives a *NO*-derivative, m.p. 121—122° (decomp.), and is converted by distillation with Zn dust into skatole. H. W.

Ergot alkaloids. X. Ergotamine and ergoclavine. W. A. JACOBS and L. C. CRAIG (J. Org. Chem., 1936, 1, 245—253; cf. A., 1936, 764, 872).—Hydrolysis (a) by NaOH , followed by HCl , and (b) by HCl alone shows that ergotamine is derived from lysergic acid (I), NH_3 , *d*-proline (II), *l*-phenylalanine (III), and AcCO_2H . Since (II) is obtained also by hydrolysis of ergotoxine, its production is not due to isomerisation during hydrolysis. Although analysis of ergoclavine (IV), anhyd. and $+\text{EtOH}$, m.p. 176—177° (to a turbid resin) after sintering at 175°, $[\alpha]_D^{25} +104^\circ$ in CHCl_3 , indicates a formula $\text{C}_{31}\text{H}_{37}\text{O}_5\text{N}_5$, it is more probably $\text{C}_{25}\text{H}_{30}\text{O}_4\text{N}_4$, since hydrolysis by methods (a) and (b) gives (I), NH_3 , *l*-leucine, and AcCO_2H ; small amounts of (III) and $\text{COPr}^\beta\cdot\text{CO}_2\text{H}$ are also formed from ergotamine present as impurity. (IV) may be a mixture of isomerides or belong to a third isomeric group. R. S. C.

Aconitum alkaloids. XI. Constitution of Aconitum alkaloids. R. MAJIMA and K. TAMURA (Annalen, 1936, 526, 116—129).—Demethylation of aconine (I) by HI (*d* 1·7) at 130—140° gives a non-cryst. product which does not yield a perchlorate, aurichloride, or platinichloride, affords a non-cryst. *Ac* derivative, m.p. about 160° after softening at 130°, and evolves NH_2Et with a little NH_2Me when heated with $\text{KOH}\cdot\text{MeOH}$ at 230—240°. N of (I) is therefore united to Et, not Me as assumed previously; this is confirmed by the isolation of NMe_3EtI in the determination of NAlk (Willstätter). Oxidation of (I), aconitine (II), or jesaconitine by KMnO_4 gives MeCHO and (II) with CrO_3 gives 0·94 mol. of AcOH , all of which appear to be derived from NEt . Mesaconitine (III) has CH_2 less than (II) and when demethylated and treated with alkali it yields NH_2Me ; since when oxidised it affords CH_2O , it contains NMe . Oxidation of (II) and (III) by KMnO_4 gives the same oxonotine (IV); the thus expected presence of NH is verified by the production of NH_3 by demethylation followed by fission. (IV) is therefore $\text{C}_{32}\text{H}_{41}\text{O}_{12}\text{N}$. Hypaconitine gives CH_2O when oxidised by KMnO_4 . It yields *acetylhyponitrine*, decomp. 197—200°, which contains four acyl residues (3 *Ac*, 1 *Bz*). It therefore contains NMe in place of NEt and 1 *OH* less than (II). "Tetra-acetylaconine" is shown to be *penta-acetylaconine*. The residue obtained by treatment of (I) with $\text{KOH}\cdot\text{MeOH}$ contains basic, neutral, and acidic products, from the last of which α -hydroxyisovaleric acid is separated. H. W.

Alkaline degradation of strychnine. R. G. CLEMO (J.C.S., 1936, 1695—1698).— KOH degradation of strychnine gives three bases, $\text{C}_8\text{H}_{13}\text{N}$, b.p. 48°/1 mm. (A; *picrate*, m.p. 143—144°), $\text{C}_{10}\text{H}_{11}\text{N}$, b.p. 90°/1 mm. (B; *picrate*, m.p. 192°), and $\text{C}_{10}\text{H}_{12}\text{N}_2$, m.p. 101—102° [C; *picrate*, m.p. 253—254° (decomp.)]; *hydro*-

chloride, m.p. 248—249°]. *A* is reduced (H_2) to a base, $C_8H_{17}N$, b.p. $<40^\circ/1$ mm. [*picrolonate*, m.p. 233—234° (decomp.)]. *B* is reduced to a base, $C_{10}H_{19}N$, b.p. $65^\circ/1$ mm. [*picrate*, m.p. 147—148°; *picrolonate*, m.p. 243—246° (decomp.)]; *methiodide*, m.p. 263—264°, and is dicyclic. *C* is 3- β -aminoethylindole (tryptamine), but is isolated in a form differing from that obtained by its synthesis. Indole and 3-ethylindole have been isolated from the non-basic compounds formed in the degradation.

F. R. S.

Strychnos alkaloids. XCI. Isomerisation of bromo- and of benzylidihydro-strychnine. H. LEUCHS and H. HÖHNE (Ber., 1936, 69, [B], 2525—2530).—Interaction of bromostychnine (I) with PhCHO in boiling EtOH containing NaOEt gives *benzylidenebromostychnine*, m.p. 239—241°, $[\alpha]_D^{20} -533^\circ/d$ in $CHCl_3$, reduced (Na-Hg in MeOH) to benzylstrychnine and hydrogenated (PtO_2 in 50% AcOH) to benzylidihydrostrychnine. (I) is reduced by Na-Hg in MeOH to strychnine and by H_2 (PtO_2 in AcOH) to dihydrostrychnine (II), whilst (II) is obtained by either method from *bromodihydrostrychnine* (III), m.p. 202—204°, $[\alpha]_D^{20} -41^\circ/d$ in $CHCl_3$ (*hydrobromide*, m.p. 230—245° after softening at 225°), obtained by the action of Br in H_2O on the hydrobromide of (II). (III) and PhCHO afford *isobenzylidenedihydrostrychnine* (IV), m.p. 234—235°, $[\alpha]_D^{20} -675.8^\circ/d$ in $CHCl_3$, which is not oxidised by $KMnO_4$ in $COMe_2$, does not yield a cryst. methiodide, and is not isomerised by NaOEt in EtOH; it gives a non-cryst. Ac derivative (*methiodide*, decomp. about 275°) and is hydrogenated (PtO_2 in 50% AcOH) to *isobenzylidenedihydrostrychnine*. (III) is isomerised by NaOMe in boiling MeOH to *isobromodihydrostrychnine* I (V), m.p. 219°, $[\alpha]_D^{20} -54.3^\circ/d$ in $CHCl_3$ (*hydrochloride*; *perchlorate*), also obtained by bromination of *isodihydrostrychnine*; with PhCHO it yields (IV), it is hydrogenated to *isodihydrostrychnine* I, and gives an Ac derivative, m.p. 197—199°, $[\alpha]_D^{20} -49^\circ/d$ in $CHCl_3$. More drastic conditions of isomerisation lead to *isobromodihydrostrychnine* II, m.p. 254—269° (vac.), $[\alpha]_D^{20} -247^\circ/d$ in $CHCl_3$ (*hydrochloride*), hydrogenated to a compound $C_{21}H_{24}O_2N_2$, m.p. 298—300°, $[\alpha]_D^{20} -270^\circ/d$ in $CHCl_3$. When heated at 235—240°/vac. (III) passes into (V). (I) is isomerised to *isobenzylidihydrostrychnine*, m.p. about 130°, $[\alpha]_D^{20} -150^\circ$ in abs. EtOH (*methiodide*, m.p. 290°).

H. W.

Conessine series. II. Relationship between N-stability and pharmacological action of conessine and isoconessine. S. SIDDIQUI, R. H. SIDDIQUI, and S. K. SHARMA (Proc. Indian Acad. Sci., 1936, 4, A, 283—290).—*isoConessine* (I) with $BrCN \cdot Et_2O$ gives its hydrobromide and *dimethobromide*, m.p. 316°, *cyanoisonorisoconessine* (II), m.p. 116—117° [*hydrochloride* (+ $1\frac{1}{2}HCl$), m.p. 259—260°; *platinichloride*, m.p. 210—215° (decomp.); *aurichloride*, m.p. 190°; *hydrobromide* (III), m.p. 269—270°; *picrate*, m.p. 173—175°], hydrolysed to *isonorisoconessine*, and some *dicyanoisoconimine* (IV), m.p. 132—133°, hydrolysed to *isoconimine*. (II) $BrCN \cdot EtOAc$ gives (III) and (IV). The corresponding reactions of conessine (V) with $BrCN$ occur much more

slowly (cf. lit.). (I) with $MeI \cdot COMe_2$ gives its *dimethiodide*, m.p. 330—334°, which with $Ag_2O \cdot H_2O$ gives *isoconessinedimethylammonium hydroxide* (corresponding *picrate*, m.p. 220°, *chloride* (VI), m.p. 297—298°, and *platinichloride*, m.p. 259°), which at 200° (Hofmann degradation) gives (I), also obtained when (VI) is distilled at $310^\circ/4$ mm. Dry distillation of conessinedimethylammonium hydroxide [corresponding *picrate*, m.p. 260° (decomp.), *chloride* (VII), m.p. 284 (decomp.), $[\alpha]_D^{20} +15^\circ$, and *platinichloride*, m.p. 247° (decomp.)] gives NMe_3 , (V), *apoconessine*, and MeOH. Dry distillation of (VII) at $340^\circ/4$ mm. and of conessine dimethochloride gives (V). The greater pharmacological action of (I) as compared with that of (V) is considered to be associated with the smaller stability of its *N*-Me and the greater stability of its own nucleus.

H. G. M.

Alkaloids of Sinomenium and Cocculus. XXXVIII. Alkaloid of Stephania cepharantha, Hayata. 2. H. KONDO and I. KEMATSU (J. Pharm. Soc. Japan, 1935, 55, 121—132).—A series of degradative experiments on cepharanthine, which may be identical with pheanthine-*A*-methine (Santos, A., 1932, 664), are described.

CH. ABS. (r)

Fruits of Solanum xanthocarpum. I. Z. SAIYED and D. D. KANGA (Proc. Indian Acad. Sci., 1936, 4, A, 255—260).—Extraction of the dried fruits with light petroleum gives an oil and a sterol, *carpsterol*, $C_{30}H_{51}O_4$, m.p. 248° (Ac derivative, m.p. 193—194°), whilst extraction with EtOH gives a gluco-alkaloid, *solancarpine*, $C_{44}H_{77}O_{19}N$, m.p. 288—289° (decomp.), hydrolysed by 5% H_2SO_4 (100°; 2—3 hr.) to the alkaloid, *solancarpidine*, $C_{26}H_{43}O_3N$, m.p. 197—198° [*hydrochloride*, m.p. 313—314° (decomp.)]; *hydrobromide*, m.p. 307—208° (decomp.); *hydriodide*, m.p. 283—284° (decomp.); *sulphate*, m.p. 293—294° (decomp.); *nitrate*, m.p. 271—272° (decomp.); *H oxalate*, m.p. 238—239° (decomp.); *H tartrate*, m.p. 224—225° (decomp.); *picrate*, m.p. 148—149°, and glucose, rhamnose, and another hexose, probably galactose. This extract also contained KCl.

H. G. M.

Identity of ungernine with tazettine. E. SPÄTH, A. OREKHOV and F. KUFFNER (Ber., 1936, 69, [B], 2446—2447).—Direct comparison shows that ungernine (A., 1936, 618) is identical with tazettine and is therefore $C_{18}H_{21}O_5N$; it is suggested that the use of the name ungernine should be discontinued.

H. W.

Reineckates of heterocyclic bases. H. CARLSOHN and P. NEUMANN (J. pr. Chem., 1936, [ii], 147, 38—42).—*Reineckates* of 2 : 4- and 2 : 6-di- and 2 : 4 : 6-trimethylpyridine, *isoquinoline*, *quinoline*, *narcotine*, *papaverine*, *nicotine*, *cinchonine*, and *codeine* are prepared and their solubilities determined. All are more sol. in $COMe_2$ than in other solvents.

R. S. C.

Manufacture of arsenobenzenesulphoxylates.—See B., 1936, 1180.

Aryl mercuric heterocyclic carboxylates.—See B., 1936, 1235.

Preparation of organic mercurials from diazonium borofluorides. M. F. W. DUNKER, E. B. STARKEY, and G. L. JENKINS (J. Amer. Chem. Soc.,

1936, 58, 2308—2309).— HgArCl are obtained when diazonium borofluorides (best prepared from NH_2Ar and NaNO_2 in 50% HBF_4) mixed with HgCl_2 (in COMe_2) are added slowly to a mixture of HgCl_2 and (usually) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in aq. COMe_2 . The following are prepared: HgPhCl ; $p\text{-SO}_3\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{HgCl}$; o - and $p\text{-CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{HgCl}$; 5-chloromercurisalicylic acid; $p\text{-chloromercuridiphenyl}$, m.p. 329° (decomp.).

H. B.

Nitration of phenyl selenocyanate. F. CHALLENGER and D. I. JAMES (J.C.S., 1936, 1609—1614).—As anticipated (A., 1930, 332) the $o:p$ ratio for the nitration of PhSeCN (I) (27:73) is $>$ that for PhSCN (1:4). At -10° with 98% H_2SO_4 and HNO_3 (d 1.41) only o - and p -mononitration of (I) occurs together with some oxidation of (I) and its NO_2 -derivatives to the corresponding seleninic acids: the above ratio 27:73 has been corr. for the greater rate of oxidation of o - (II) as compared with $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SCN}$ (III). Velocity coeffs. for this oxidation of (II) and (III) at various temp. between -10° and 10° are recorded. (II) with H_2SO_4 alone is slightly hydrolysed at room temp. to $o\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SeO}_2\text{H}$, reduced by SO_2 to $(o\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Se})_2$, m.p. 215° (lit. 209°), whilst (III) is not attacked at -10° but extensively decomposed to $(p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Se})_2$, m.p. 183° (lit. 177°). It is concluded that, under the above conditions of nitration, diselenide formation does not occur and that the observed oxidations are direct. (I) with HNO_3 (d 1.485)– H_2SO_4 at -10° gives $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SeO}_2\text{H}$ and some 2:4:1-(NO_2) $_2\text{C}_6\text{H}_3 \cdot \text{SeO}_2\text{H}$, m.p. $168\text{--}3^\circ$ (lit. 163°), whilst (II) and (III) at -15° give only the corresponding seleninic acids. PhSO_2H and also $p\text{-C}_6\text{H}_4\text{R} \cdot \text{SeO}_2\text{H}$ ($\text{R} = \text{NO}_2$, Cl , or Br) give an intense blue colour with cold $\text{H}_2\text{SO}_4\text{--NHPh}_2$.

H. G. M.

Organo-metalloid compounds. I, II. S. NIXOGY (Proc. Indian Acad. Sci., 1936, 4, A, 303—308, 309—313).—I. Nitration of *acetophenone-4-stibinic acid* (Na salt), obtained from $p\text{-NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COMe}$ by diazotisation and subsequent treatment with $\text{SbCl}_3\text{--HCl}$, gives its 2- NO_2 -derivative (I), the *semicarbazone* of which is reduced (Hg--Al) to 2-*aminoacetophenone-4-stibinic acid semicarbazone* (Na salt). This is hydrolysed to the *ketone* (Na salt; *hydrochloride*), which is converted by the diazo-reaction into 2-*hydroxyacetophenone-4-stibinic acid* [Na salt; *semicarbazone* (II)]. The constitution of (I) was established by conversion with $\text{KI--H}_2\text{SO}_4$ into 2:4:1- $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{I} \cdot \text{COMe}$, from which $m\text{-C}_6\text{H}_4\text{I} \cdot \text{NO}_2$ was obtained. The physiological activity of (II) in cases of kala-azar is slight only.

II. The following were prepared from the appropriate diazotised amine and $\text{SbCl}_3\text{--HCl}$: *benzyl alcohol-4-* (Na salt, decomp. 220° ; Ca and Ba salts), -3- (Na salt), and -2-*stibinic acid*; 2-*acetamidobenzyl alcohol-5-stibinic acid* (Na , Ca , and Ba salts); 3-*nitrobenzyl alcohol-4-stibinic acid* (Na salt), reduced by $\text{FeSO}_4\text{--NaOH--H}_2\text{O}$ to 3-*aminobenzyl alcohol-4-stibinic acid* (Na salt, decomp. 230° ; Ca salt; Ac derivative). 5-*Amino-2-acetamidobenzyl alcohol*, m.p. $172\text{--}173^\circ$, is obtained by reduction of the corresponding 5- NO_2 -compound with $\text{Fe--AcOH--H}_2\text{O}$.

H. G. M.

Production of thyroxine by iodination of protein. W. LUDWIG and P. VON MUTZENBECHER (Z. physiol. Chem., 1936, 244, IV).—When protein is treated gradually with I at moderately high temp. and feebly alkaline reaction and the I -compounds produced are degraded after dialysis and pptd. with acid, thyroxine and substances slightly less active are obtained.

W. McC.

Organic micro-analysis. II. Drying and analysis of hygroscopic substances. R. T. MILLNER and M. S. SHERMAN (Ind. Eng. Chem. [Anal.], 1936, 8, 427—428).—Modifications are described in a micro-drying apparatus whereby the sample (I) is transferred to the balance without coming in contact with air. Before combustion, (I) is equilibrated with air; the increase in wt. (H_2O) is then allowed for.

J. L. D.

Modified Mariotte flask for the Pregl C-H determination. O. G. BACKEBERG (Mikrochem., 1936, 21, 135—137).—The modifications introduced eliminate repeated adjustment of the siphon tube to ensure steady flow of gases during combustions.

J. W. S.

Determination of oxygen in organic compounds containing sulphur. Ter Meulen method. W. W. RUSSELL and M. E. MARKS (Ind. Eng. Chem. [Anal.], 1936, 8, 453—455; cf. A., 1934, 90).—Pt-coated SiO_2 granules forms an efficient "cracking" catalyst and holds back most of the S compounds which poison the Ni or Ni--ThO_2 hydrogenation catalyst. If the latter is deposited on SiO_2 the blank correction due to the reduction of traces of NiO by H_2 is small and const. The catalyst cannot be regenerated. Improvements in technique are described.

J. L. D.

Semi-micro-determination of acetyl, especially in O -acetyl compounds. E. P. CLARK (Ind. Eng. Chem. [Anal.], 1936, 8, 487—488).—The sample (10—20 mg.) is hydrolysed with boiling N-KOH in EtOH and diluted with $\text{MgSO}_4\text{--H}_2\text{SO}_4$. Distillation with steam at const. vol. removes 95.7% of the AcOH in the sample. N-Ac compounds require longer boiling with N-KOH in Bu°OH . The method cannot be applied in cases where the hydrolytic products, other than AcOH , are volatile in steam and interfere with the titration.

J. L. D.

Micro-determination of carbamide.—See A., III, 52.

Determination of camphor. V. E. TISCHTSCHENKO and M. A. GRECHNEV (J. Appl. Chem. Russ., 1936, 9, 1700—1703).—0.6—0.8 g. of camphor (I) is added to one of two flasks each containing 1.2 g. of NaHCO_3 and 21 ml. of a solution of 20 g. of $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 30 ml. of H_2O and 125 ml. of EtOH , and the flasks are heated under reflux at 75° for 2 hr. The cooled contents are diluted to 500 ml., filtered, and 25-ml. portions are titrated with 0.2N- HCl (Me-orange). The difference in the vols. of acid used corresponds with the amount of NH_2OH combined with the (I), the % content of which is hence calc.

R. T.

Determination of glyoxaline.—See A., III, 10.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1937.

Mechanism of the photochemical decomposition of methane.—See A., I, 91.

Free radicals and atoms in primary photochemical processes. Free propyl radical from diisopropyl ketone. H. G. GLAZE BROOK and T. G. PEARSON (J.C.S., 1936, 1777—1779).—On exposure to ultra-violet light, COPr^{β}_2 yields free *iso*(?)propyl which with Hg gives HgPr^{α}_2 . The half-life periods of Pr^{α} and Pr^{β} are 4.0 and 4.4×10^{-3} sec., respectively.

F. N. W.

Catalytic polymerisation of ethylene at atmospheric pressure. I, II. Y. KONAKA (J. Soc. Chem. Ind. Japan, 1936, 39, 447B).—I. No polymerisation occurs in presence of Al_2O_3 , SiO_2 gel, or Cu, but with Co or Ni at 350° a colourless liquid and C result; the latter is much reduced in amount by Cu. ThO_2 , U_3O_8 , TiO_2 , Al_2O_3 , and ZnO promote the activity of Co slightly.

II. The Co catalyst is best prepared from CoO which is obtained from CoCO_3 or $\text{Co(NO}_3)_2$. 300° is the optimum temp. of polymerisation; above 300° much H_2 , CH_4 , and C are formed. Co deposited on kieselguhr has a longer life than the unsupported catalyst.

J. L. D.

Reactions between ethylene and halogens and their products. A. SHERMAN, O. T. QUIMBY, and R. O. SUTHERLAND (J. Chem. Physics, 1936, 4, 732—740; cf. A., 1934, 736).—Theoretical considerations indicate that (1) Cl_2 , Br, and I will tend to give symmetrical additive products with C_2H_4 ; (2) HCl and HBr will combine with the corresponding vinyl compound rather than react to give C_2H_4 and halogen, whilst the I compounds will react in both ways; (3) decomp. of *s*- or *as*- $\text{C}_2\text{H}_4\text{Br}_2$ or $\text{C}_2\text{H}_4\text{I}_2$ will give rise to C_2H_4 and Br or I, whereas $\text{C}_2\text{H}_4\text{Cl}_2$ will give HCl and $\text{CH}_2=\text{CHCl}$; (4) usually mechanisms involving free radicals are more probable than the corresponding uni- or bi-mol. reactions.

F. L. U.

Addition of hydrogen halides to butadiene. S. N. GANGULY (J. Indian Chem. Soc., 1936, 13, 580—585).—Addition of anhyd. HBr to butadiene gives α -bromo- Δ^{β} -butene only. With HCl β -chloro- Δ^{γ} - and α -chloro- Δ^{β} -butene are formed: the absence of any α -chloro- Δ^{γ} -butene was not established, and attempts to prepare this compound from allylcarbinol failed.

H. G. M.

Addition of hydrogen bromide to allyl bromide in the presence of various substances. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1936, 11, 692—694; cf. A., 1933, 805).—Interaction of HBr and $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Br}$ in the presence of air, reduced Fe, or reduced Ni affords $\text{CH}_2(\text{CH}_2\text{Br})_2$

principally, whilst in the presence of S, NO, Pt-black, FeBr_2 , or MnSO_4 the production of $\alpha\beta$ -dibromopropane is favoured. Fe, Ni, and Pt alone increase the total yield.

F. N. W.

Addition of hydrogen bromide to allyl bromide in presence of various substances. II. Effects of ferro-magnetic catalysts. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1936, 11, 754—756).—Reduced Fe and Ni in presence of NHPh_2 accelerate the abnormal addition of HBr to allyl bromide and afford chiefly $\text{CH}_2(\text{CH}_2\text{Br})_2$. Co, Fe-sand, and surface-oxidised Ni have no influence on the normal addition.

J. D. R.

Photochemical formation of carbonyl chloride from chloroform, chlorine, and oxygen.—See A., I, 91.

Rearrangements of α -propylcrotyl chloride and phenyl α -propylcrotyl ether. C. D. HURD and J. W. WILLIAMS (J. Amer. Chem. Soc., 1936, 58, 2636—2637).—The previously prepared (A., 1931, 838) α -propylcrotyl chloride [β -chloro- Δ^{β} -heptene], Ph α -propylcrotyl ether (I), and *o*- α -methyl- Δ^{β} -hexenylphenol (II) are shown (by ozonolysis) to contain about 20% of their respective isomerides, viz., β -chloro- Δ^{γ} -heptene (formed by anionotropic change), Ph α -methyl- Δ^{β} -hexenyl ether, and *o*- α -propylcrotylphenol. The rearrangement of (I) into (II) involves an inversion of the propylcrotyl group, thus supporting the view that allyl undergoes inversion during rearrangement of Ph allyl ether to *o*-allylphenol.

H. B.

Constitution of tetranitromethane. R. ROBINSON (Nature, 1936, 138, 975—976).—Arguments in favour of $\text{C(NO}_2)_4$ and against the proposed revision (*ibid.*, 807) are advanced.

L. S. T.

Preparation of tetranitromethane. C. KRAUZ and J. ŠTEPÁNEK (Chem. Obzor, 1935, 10, 137—140; Chem. Zentr., 1936, i, 1707).—An improved prep. (95% yield) from N_2O_5 and Ac_2O is described. Nitration of COMe_2 with fuming HNO_3 yields *acetylmethylnitrolic acid* (Ag salt). $\text{C(NO}_2)_4$ and KOEt, followed by decomp. with H_2SO_4 , yield $\text{CH(NO}_2)_3$.

H. N. R.

Bromination of acetylene in light.—See A., I, 91.

Differentiation of monohydric primary, secondary, and tertiary alcohols. Micro-determination of velocity of esterification. S. MURAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 272—277).—2—5 mg. of alcohol and pure $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ (1 mol.) are heated at 155 — 156° for 1 hr. The free acid is then titrated with 0.01N-NaOH.

The % esterification is for *n*-nonyl and -hexyl alcohol and tetrahydrogeraniol 57.8—62.3, for *sec*-octyl and -butyl alcohol, 24.5—30.6, and for Bu^oOH, linalool, and tetrahydrolinalool 1.1—12.1. R. S. C.

Detection and approximate determination of primary in the presence of secondary and tertiary alcohols by the formation of triphenyl-methyl ethers. S. SABETAY (Compt. rend., 1936, 203, 1164—1166).—CH₂R·OH with excess of CPh₃Cl in boiling dry PhMe affords a CPh₃ ether (>80%) and HCl which can be removed by CO₂ and determined titrimetrically. CHR₂·OH and CR₃·OH in the same period react to <25% and <5%, respectively. By choosing a suitable reaction period the method is approx. quant. J. L. D.

Exchange of hydrogen between ethyl alcohol and calcium deuterioxide.—See A., I, 81.

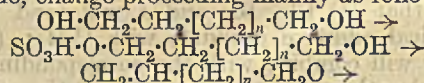
Electrolytic oxidation of alcohols and aldehydes in alkaline solution. T. KURENNIEMI and E. TOMMILA (Suomen Kem., 1936, 9, B, 25—26).—Pr^oOH has been oxidised at 20° on smooth Pt anodes in 1—4*N*-NaOH with a good yield, which decreases with NaOH of concn. >4*N*. The anodic gas consisted of 80—90% of C₂H₄, 3—10% of CH₄ and C₂H₆, O₂, and CO; the anolyte contained EtCHO and a good yield of HCO₂H, EtCO₂H, and CO₂. EtCHO gave O₂, a little CO, C₂H₄, and HCO₂H, and mainly EtCO₂H. In 1—2*N*-NaOH, Pr^oOH gave COMe₂, Bu^oOH and Bu^oOH gave mainly unsaturated hydrocarbons, HCO₂H, and the corresponding fatty acids, and a little unsaturated hydrocarbons. On Fe and Ni electrodes the respective fatty acids were obtained with traces of the above side products. The aldehydes probably act either in the hydrated or in the enolic form: CHR(OH)₂ + O = RCO₂H + H₂O (i) and CHR:CH·OH + O → R·CH·OH·CH>O → OH·CHR·CHO → OH·CHR·CH(OH)₂ → RCHO + HCO₂H + H₂O (ii). Reaction (ii) is not observed with Fe and Ni, since oxidation is milder on these electrodes than on Pt. Pr^oOH produces considerable yields of HCO₂H in contrast to EtCHO because with the former EtCHO is oxidised before it can hydrate. R. S. B.

Stereochemical relationships of isomeric butane-βγ-diols and related compounds; evidence of Walden inversion. C. E. WILSON and H. J. LUCAS (J. Amer. Chem. Soc., 1936, 58, 2396—2402).—The mixture (I) of *cis*- and *trans*-Δ^β-butene obtained by dehydration (H₂SO₄) of Bu^oOH is converted (aq. HOCl) into a mixture, b.p. 50—60°/30 mm., of γ-chlorobutan-β-ols; this with aq. KOH at 90° gives an approx. 35 : 65 mixture of *cis*- (II), b.p. 59.9—60.4°/747 mm., and *trans*- (III), b.p. 53.6—54.1°/747 mm., -βγ-oxidobutanes, thus confirming the composition (A., 1930, 888) of (I). (II) and (III) are slightly impure but subsequent hydration (aq. HClO₄) affords the diols which are purified by crystallisation; (II) thus yields *dl*-butane-βγ-diol (IV), b.p. 86°/16 mm., 176.7°/742 mm., m.p. 7.6° [diacetate (V), b.p. 70°/5.5 mm., m.p. 41—41.5°; dibenzoate, m.p. 53—54°; *di-p*-bromobenzoate, m.p. 205—209°], whilst (III) furnishes *meso*-butane-βγ-diol (VI), b.p. 89°/16 mm., 181.7°/742 mm., m.p. 34.4° [diacetate (VII), b.p.

66°/5.5 mm., m.p. 2.5—3°; dibenzoate, m.p. 75.5—76.2°; *di-p*-bromobenzoate, m.p. 139—139.8°]. The f.-p. curve for (IV) and (VI) is given. (IV) and (VI) undergo a pinacol rearrangement (COMeEt isolable) with conc. HBr but (V) and (VII) similarly give *meso*-, b.p. 73.2—73.4°/50 mm., and *dl*-, b.p. 76.4—76.6°/50 mm., -βγ-dibromobutane, respectively, which are debrominated (Zn) to *trans*- (VIII) and *cis*- (IX) -Δ^α-butene, respectively. The above reactions afford a method for the interconversion of (VIII) and (IX). It is proved (below) that the change (III) → (VI) occurs through a Walden inversion, and it is believed that five inversions occur in, e.g., the conversion of (VIII) into (IX), viz., (VIII) → chlorhydrin → (III) → (VI) → (VII) → *dl*-dibromide → (IX).

(II) and (III) with aq. NHMe₂ at 100° give *dl*-threo-, b.p. 141—142°/743 mm., and *dl*-erythro- (X), b.p. 152.5—153.5°/743 mm., -γ-dimethylaminobutan-β-ol, respectively, the methiodides of which with Ag₂O-H₂O followed by distillation regenerate (II) and (III), respectively. The methohydroxide from (X) is resolved (partly) through the *tartrate*, [α]_D²⁰ +19.1°; similar decomp. affords an active oxide [i.e., (III)] (not isolated), which is hydrated to an inactive glycol [i.e., (VI)]. The configurations of (IV) and (VI) are established by the formation of (VI) from the optically active (III), by the production of optically active (IV) when (II) is hydrated in presence of *d*-tartaric or *d*-camphorsulphonic acid (XI) [(III) similarly gives (VI)], and by the isolation of an active fraction which has not reacted when (IV) is partly esterified with (XI). H. B.

Cyclic ethers from glycols. A. FRANKE and A. KROUPA [with F. SCHWEIZER, M. WINISCHOFER, H. KLEIN-LOHR, M. JUST, M. HACKL, I. VON REYHER, and R. BADER] (Monatsh., 1936, 69, 167—203).—The action of 55% H₂SO₄ on diols containing the OH groups in αζ or more distant positions gives very little ωω'-oxide, change proceeding mainly as follows:



CH₃·CH(O·SO₃H)·[CH₂]_n·CH₂·OH and so onwards until the OH are in a position favourable for ring-closure. Oxidation of the products with CrO₃ gives small amounts of the corresponding CO-acids, but mainly fatty acids and (·CH₂·CO₂H)₂, whilst much unchanged product remains; KMnO₄ gives less satisfactory results. The constitution of the products is therefore determined by their transformation by conc. HBr into the corresponding dibromides, thence into the dinitriles and dicarboxylic acids, which are separated from one another through their mono- or diamides. The product obtained from hexane-αζ-diol and 57% H₂SO₄ at 133° contains about 10% of αζ-, 25% of αε-, and 65% of αδ-oxido-hexane. Heptane-αη-diol gives about 33% of αδ-oxido-heptane, b.p. 128—131.5°. Octane-αθ-diol gives about 70% of αδ- and 30% of αε-oxido-octane. Undecane-ακ-diol, undecane-αλ-diol, undecylenyl alcohol, and undecene-αλ-diol give the same *oxide*, b.p. 220—223°. Decane-ακ-diol and dodecane-αμ-diol give mainly αδ-oxido-decane and -dodecane, respectively. The following substances are prepared for purposes of comparison.

$\text{CHEt}(\text{CO}_2\text{Et})_2\text{Na}$, and $\text{CH}_2(\text{CH}_2\text{Br})_2$ give Et_2 ethyl- γ -bromopropylmalonate (I), b.p. 152—156°/9 mm., whence Et_2 ethyl- γ -cyanopropylmalonate, b.p. 171—174°/10 mm., hydrolysed by $\text{KOH-EtOH-H}_2\text{O}$ to *n*-hexane- $\alpha\delta\delta$ -tricarboxylic acid, m.p. 150° (decomp.), decarboxylated at 180° to α -ethyladipic acid, b.p. 166—167°/1 mm., m.p. 53° (diamide, m.p. 180°; monoamide, m.p. 135.4°). Similarly Et_2 propyl- γ -bromopropylmalonate (II), b.p. 162—166°/11.5 mm., affords successively Et_2 propyl-*n*-cyanopropylmalonate, b.p. 179—182°/10.5 mm., *n*-heptane- $\alpha\delta\delta$ -tricarboxylic acid, and α -propyladipic acid, b.p. 182—183°/1 mm., m.p. 56° (diamide, m.p. 181.2°; monoamide, m.p. 146.8°). Et_2 γ -bromopropyl-*n*-butylmalonate, b.p. 171°/10.5 mm., affords Et_2 γ -cyanopropyl-*n*-butylmalonate, b.p. 153—156°/1 mm., *n*-octane- $\gamma\delta\delta$ -tricarboxylic acid, m.p. 171° (decomp.), and *n*-butyladipic acid, b.p. 176°/0.25 mm., m.p. 63° (diamide, m.p. 180.9°; monoamide, m.p. 142.2°). $\alpha\epsilon$ -Dibromohexane yields the corresponding dinitrile, b.p. 162—168°/11 mm., hydrolysed by alkali to α -methylpimelic acid, b.p. 166°/1 mm., m.p. 55° (diamide, m.p. 151°). (I) and $\text{CHNa}(\text{CO}_2\text{Et})_2$ afford Et_4 *n*-heptane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylate, b.p. 220—222°/13 mm., hydrolysed to *n*-heptane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylic acid, which passes at 180° into α -ethylpimelic acid, b.p. 210—211°/9 mm., m.p. 42.3° (diamide, m.p. 161—162°; monoamide, m.p. 108—109°). Similarly, (II) and $\text{CHNa}(\text{CO}_2\text{Et})_2$ afford successively Et_4 *n*-octane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylate, b.p. 195.5—197°/0.75 mm., *n*-octane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylic acid, and α -propylpimelic acid, b.p. 212°/3 mm., m.p. 61.5° (diamide, m.p. 150.2°). Bu^nBr is transformed by Mg and trioxymethylene into *n*-amyl alcohol, whence the bromide and Et_2 *n*-amylmalonate, b.p. 124—125°/9 mm., which gives Et_2 γ -bromopropyl-*n*-amylmalonate, b.p. 175—178°/8 mm. This with $\text{CHNa}(\text{CO}_2\text{Et})_2$ affords Et_4 *n*-decane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylate, b.p. 225—228°/8 mm.; the corresponding acid passes at 200° into α -*n*-amylpimelic acid, b.p. 232—234°/11 mm. (diamide, m.p. 164.2°; monoamide, m.p. 109.4°). *n*-Heptyl alcohol, obtained by reducing heptaldehyde with Al-Hg in EtOH, gives the bromide and thence successively Et_2 *n*-heptylmalonate, b.p. 146—149°/9 mm., Et_2 γ -bromopropyl-*n*-heptylmalonate, b.p. 161—165°/1 mm., Et_4 *n*-dodecane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylate, the corresponding free acid, and *n*-heptylpimelic acid, b.p. 190—193°/1 mm., m.p. 60° (diamide, m.p. 166.4°; monoamide, m.p. 110°). The semicarbazone, m.p. 170° (block), of γ -keto-*n*-hexoic acid, m.p. 41—42°, is described. Et heptoylacetate, Na, and $\text{CH}_2\text{Br-CO}_2\text{Et}$ yield Et_2 heptoylsuccinate, b.p. 130—134°/0.5 mm., converted by conc. HCl in boiling AcOH into γ -keto-*n*-decoic acid, m.p. 70°. Et propionylacetoacetate is transformed by Na and $\text{CH}_2\text{I-CH}_2\text{-CO}_2\text{Et}$ into Et_2 α -propionylglutarate, b.p. 150—152°/9 mm., hydrolysed by boiling HCl (1:2) to δ -ketoheptonic acid, b.p. 152—153°/9 mm., m.p. 50° [Ag salt; semicarbazone, m.p. 193° (block; decomp.)]. Et_2 α -butyrylglutarate, b.p. 161—163°/10.5 mm., gives δ -keto-octonic acid, b.p. 156—162°/10 mm., m.p. 35° [Ag salt; semicarbazone, m.p. 195° (block; decomp.)]. Et_2 α -valerylglutarate, b.p. 115—125°/0.5 mm., yields δ -ketonononic acid, m.p. 43.5° [Ag salt; semicarbazone, m.p. 142° (block)]. Et hexoylacetate (*Cu* derivative, m.p. 107°) affords Et_2 α -hexoylglutarate, b.p. 140—

2* (A., II.)

142°/0.2 mm., whence δ -ketodecoic acid, b.p. 155—161°/2 mm., m.p. 56.5° (Ag and Ba salts; semicarbazone, m.p. 126°). Et_2 α -heptoylglutarate, b.p. 130—136°/0.5 mm., gives δ -ketoundecoic acid, m.p. 60° (Ag and Ba salts; semicarbazone, m.p. 132.5°).

Decan- α -ol- ϵ -one is converted by conc. HBr at 70° into ϵ -ketodecyl bromide, b.p. 140—146°/10 mm., transformed by $\text{NH}_3\text{-EtOH}$ into 2-*n*-amyl- Δ^2 -tetrahydropyridine, b.p. 94.5—95°/9 mm. (hydrochloride; platinichloride, m.p. 165.5—166°; picrate, m.p. 67°; stannochloride, m.p. 127°; non-cryst. mercurichloride; picrolonate, decomp. about 170°; perchlorate, m.p. 88.5°), reduced by Sn and conc. HCl to 2-*n*-amylpiperidine, b.p. 86.5—87°/10 mm. (hydrochloride; platinichloride, m.p. 117°; non-cryst. picrate and mercurichloride; picrolonate, m.p. 154°). Heptan- α -ol- ζ -one, b.p. 119—122°/9 mm., is converted by H_3PO_4 into substances of high mol. wt.; with HCl it appears to yield a trace of oxide but mainly unchanged material and complex compounds. ζ -Ketoheptyl bromide, b.p. 107—108°/8 mm., does not appear to react with $\text{NH}_3\text{-EtOH}$ at room temp., whereas at 60—70° it yields mainly complex bases non-volatile with steam; a seven-membered ring does not appear to be formed.

H. W.

Electrochemical preparation of nitric esters. V. ÖHMANN (Z. Elektrochem., 1936, 42, 862—872).—The prep. of several esters by electrolysis of mixtures of unsaturated org. compounds in AcOH or COMe₂ with aq. HNO_3 , NaNO_3 , or $\text{Ca}(\text{NO}_3)_2$, using a polished Pt anode, is described. The influences of concn. of org. compound, H_2O content of the anolyte, c.d., and anode material have been investigated.

E. S. H.

Reactions of alkyl sulphates, ethyl orthosilicate, and ethyl carbonate in Friedel-Crafts syntheses. H. L. KANE and A. LOWY (J. Amer. Chem. Soc., 1936, 58, 2605—2608).—The effects of time, temp., and proportions of reagents on the formation of PhAlk (I) from C_6H_6 , AlCl_3 , and various alkyl esters are investigated. The max. yields of (I) obtained are: from Me_2SO_4 59.8, Et_2SO_4 71.4, Pr^i_2SO_4 44.2, Bu_2SO_4 43.6, Et_4SiO_4 53.3, and Et_2CO_3 56.4%. Pure compounds could not be obtained from C_{10}H_8 , Et_2SO_4 , and AlCl_3 in CS_2 or *o*- $\text{C}_6\text{H}_4\text{Cl}_2$. EtCl is not formed from AlCl_3 and Et_2SO_4 or Et_2CO_3 in light petroleum.

H. B.

Esters of chlorosulphonic, sulphurous, and sulphuric acids. R. LEVAILLANT (Ann. Chim., 1936, [xi], 6, 459—581).—A compilation of 13 papers previously published (cf. A., 1935, 729, 733, and earlier abstracts).

F. N. W.

β -Octyl thiocyanate. W. G. ROSE and H. L. HALLER (J. Amer. Chem. Soc., 1936, 58, 2648—2649).— β -Octyl bromide, $[\alpha]_D^{20} -32.15^\circ$ (from *d*- β -octanol, $[\alpha]_D^{20} +9.7$, and PBr_3), and MeOH-KCN give β -octyl thiocyanate, b.p. 98.5—99°/4 mm., $[\alpha]_D^{20} +51.7^\circ$, the *d* of which is > that of the (–)-form of Kenyon *et al.* (A., 1935, 1230).

H. B.

X-Ray and thermal examination of α -mono-glycerides.—See A., I, 17.

Synthesis of glycerides. I. C. L. TSENG and M. C. CHIANG (J. Chinese Chem. Soc., 1936, 4, 463—

472).—The prep. of glycerol α -*p*-bromobenzoate (I), m.p. 74.4° (lit. 70°), and its CMe_2 derivative is modified. (I) gives the CPh_3 ether, m.p. 178.6° [hydrolysed by $\text{HBr}\cdot\text{AcOH}$ at 0° to (I)], and thence glycerol α - CPh_3 ether β -benzoate α' -*p*-bromobenzoate, m.p. 76.1—83.1°, converted by $\text{HBr}\cdot\text{AcOH}$ at 0° into glycerol β -benzoate α -*p*-bromobenzoate, a syrup, and thence into glycerol β -benzoate α -*p*-bromobenzoate α' -*p*-nitrobenzoate, m.p. 152.6°, and β -benzoate α' -*di*-(*p*-bromobenzoate), m.p. 153.1°. M.p. are corr.

R. S. C.

Tertiary oxonium salts. I. H. MEERWEIN, G. HINZ, P. HOFMANN, E. KRONING, and E. PFEIL (J. pr. Chem., 1937, [ii], 147, 257—285).—Gradual addition of epichlorohydrin (I) to $\text{Et}_2\text{O}\cdots\text{BF}_3$ in Et_2O gives a semi-solid mass (II) which on decomp. with $2\text{N}\cdot\text{Na}_2\text{CO}_3$ or H_2O affords γ -chloro- α -ethoxypropanol (III), b.p. 72—74°/13.5 mm., in 72% yield identical with the additive product from (I) and EtOH and apparently free from the isomeric β -ether. The solid portion of (II) consists of triethyloxonium borofluoride, OEt_3BF_4 (IV), whilst the ethereal mother-liquor contains γ -chloro- α -ethoxy- β -propyl borate [$\text{OEt}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\text{Cl})\cdot\text{O}$] $_3\text{B}$, b.p. 210—216°/12 mm. [converted into (III) by Na_2CO_3], with small amounts of the substance, $\text{C}_6\text{H}_{11}\text{O}_2\text{Cl}\cdot\text{BF}_3$, m.p. 108° (decomp.), also obtained from (III) and BF_3 . Addition of (I) to $\text{Me}_2\text{O}\cdots\text{BF}_3$ in Me_2O yields trimethyloxonium borofluoride (V), γ -chloro- α -methoxy- β -propyl borate, b.p. 150—152°/2 mm., and the non-homogeneous adduct of BF_3 and γ -chloro-2-methoxypropan- β -ol, b.p. 64—66°/12 mm. (V) after purification by dissolution in PhNO_2 containing SO_2 and separation by removal of the latter has m.p. 124.5° (decomp.). (IV), m.p. 92° (decomp.) greatly dependent on purity, is very hygroscopic. When pure it can be preserved for considerable periods in sealed tubes, but slightly impure specimens soon liquefy with loss of HF . When heated, (IV) dissociates into $\text{Et}_2\text{O}\cdots\text{BF}_3$ and EtF with minor amounts of gases, including C_2H_4 . The best method for the prep. of (IV) consists in the slow addition of EtF to $\text{Et}_2\text{O}\cdots\text{BF}_3$ and Et_2O in a sealed tube at room temp. $\text{Me}_2\text{O}\cdots\text{BF}_3$ and EtF unite more rapidly to dimethylethyloxonium borofluoride (VI), m.p. 120—121° (decomp.), which passes when heated into $\text{MeEtO}\cdots\text{BF}_3$ and MeF with minor amount of $\text{Me}_2\text{O}\cdots\text{BF}_3$ and EtF ; decomp. thus occurs as with mixed quaternary ammonium halides containing Me . Addition of (IV) to Na picrate gives triethyloxonium picrate, m.p. 58° (decomp.), which in contact with the mother-liquor gives picric acid and Et picrate and has limited stability when solid. Attempts to prepare triethyloxonium iodide from (IV) and NaI in COMe_2 gave NaBF_4 and EtI . The following examples of the powerful ethylating action of (IV) are described. H_2O is converted into Et_2O and EtOH in 89.2 and 89% yield, respectively. (III) and (IV) at room temp. give γ -chloro- α - β -diethoxypropane, b.p. 69.8—70.4°/14 mm., in 55% yield. PhOEt is obtained in 73% or 91.1% yield from PhOH and (IV) at room temp. or from $\text{NaOPh}\cdot\text{H}_2\text{O}$ and (IV) at 0°. AcOH and (IV) give EtOAc in 46% yield, whilst NaOBz in H_2O and (IV) afford EtOBz (yield 70.8%). Aq. NaI and (IV) give EtI (77%). Na 3:5-dinitrobenzoate and (VI)

give a mixture of 70% of Me and 30% of Et 3:5-dinitrobenzoate. $\text{CHNa}(\text{CO}_2\text{Et})_2$ in EtOH and (IV) afford $\text{CHEt}(\text{CO}_2\text{Et})_2$ in 35.8% yield, whereas $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ gives $\text{CHEtAc}\cdot\text{CO}_2\text{Et}$ (46.7%). (IV) (1 mol.) and NH_3 (1.1 mol.) give mainly NHEt_2 and NEt_3 with some NH_2Et . Gradual addition of $\text{C}_5\text{H}_5\text{N}$ to well-cooled (IV) affords Et_2O (94.3%) and 1-ethylpyridinium borofluoride, m.p. 58.5—59.5°, which does not give EtF when heated and is oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ to 1-ethylpyridone, b.p. 124—125°/13 mm. (IV) and an excess of Et_2S give triethylsulphonium borofluoride, m.p. 105.5°. 2:6-Dimethyl-4-pyrone and (IV) in CH_2Cl_2 at room temp. afford 4-ethoxy-2:6-dimethylpyrylium borofluoride, m.p. 90—91°, whence the corresponding perchlorate, m.p. 126—128°; either salt is transformed by $(\text{NH}_4)_2\text{CO}_3$ into 4-ethoxy-2:6-dimethylpyridine, m.p. 112°. Similarly (IV) and coumarin in CH_2Cl_2 give 2-ethoxybenzopyrylium borofluoride, m.p. 106° (decomp.). Camphor (VII) and

(IV) yield the compound (VIII), m.p. 104.5—105.5° (decomp.), from which H_2O regenerates (VII). $\alpha\beta$ -Unsaturated ketones such as distyryl ketone give intensely coloured salts with (IV), but differentiation between the structures $(\text{CHR}:\text{CH})_2\text{C}(\text{OEt})\cdot\text{BF}_4$ and $(\text{CHR}:\text{CH})_2\text{C}:\text{OEt}\cdot\text{BF}_4$ is not at present possible. The compound $[(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH})_2\text{C}:\text{OEt}]\text{BF}_4$ gives EtF when heated.

H. W.

Bromination of aliphatic $\alpha\alpha$ -disulphones.—See A., I, 88.

Synthesis of esters by dehydration of alcohols by copper-cerium catalysts. III. M. M. KOTON (J. Gen. Chem. Russ., 1936, 6, 1291—1294).—The condensate obtained by passing EtOH over $\text{Cu}\cdot\text{Zr}$ catalyst (0.9% Zr) at 250° contains 50% of EtOAc and 3—6% of AcOH ; the yield of EtOAc may be raised to 65% by repeating the process four times. The inactivated catalyst may be regenerated by passing air at 150—170°, followed by reduction in H_2 at 150°.

R. T.

Rates of alcoholysis of acyl chlorides.—See A., I, 87.

Reaction between esters and acid chlorides. B. Z. AMTIN and E. V. HIRSCHBERG (Proc. Charkov State Univ., 1936, 4, 55—58).—The yield of alkyl chlorides in presence of ZnCl_2 (cf. Kyrides *et al.*, A., 1934, 72) in the reactions $\text{AcCl} + \text{EtOAc}$, $\text{AcCl} + \text{C}_5\text{H}_{11}\text{OAc}$, $\text{BzCl} + \text{furyl benzoate}$, and phthalyl chloride + furyl phthalate is very small or non-existent. When an alkyl chloride is formed the corresponding unsaturated hydrocarbon seems to be an intermediate product.

J. J. B.

Preparation of trichloroacetic acid. E. S. CHOTINSKI and E. ALEXANDROVA (Proc. Charkov State Univ., 1936, 4, 59—61).— CCl_3CHO and NO_2 at 40—60° yield up to 70% of $\text{CCl}_3\text{CO}_2\text{H}$. The NO formed can be oxidised by air to NO_2 and used again.

J. J. B.

Selective hydrogenation of mixtures of unsaturated compounds.—See A., I, 90.

Fats. XXXII. Preparation of unsaturated fatty acids by debromination of their additive

products with bromine. H. P. KAUFMANN and H. E. MESTERN (Ber., 1936, 69, [B], 2684—2685).—A stream of an indifferent gas is passed through a boiling solution of the pure bromide in C_6H_5N containing Zn. After 1 hr. the mixture is poured into dil. HCl and the fatty acids are extracted with Et_2O or C_6H_{12} . Examples cited are: elaidic acid from its dibromide; linoleic and linolenic acid from tetra- and hexa-bromostearic acid, respectively; tiglic acid from its dibromide. H. W.

Fats. XXIX. Thiocyanogen iodide and its addition to unsaturated fatty acids. H. P. KAUFMANN and H. G. OETRINGHAUS (Ber., 1936, 69, [B], 2670—2676).—Interaction of inorg. thiocyanates with I in various media generally leads to the appearance of I and CNS separately, and only in $n-C_6H_{12}$ is a mixture produced which probably contains $I(SCN)$ which could not be isolated from KCNS and IBr in absence of solvent. Indications of its production when equiv. amounts of CNS and I are boiled in C_6H_6 are given by the enhanced stability of the solution; polymerisation occurs only after several hr., and then proceeds very rapidly. Gradual addition of this solution to $CHPh:CH_2$, C_2H_4 , C_2H_2 , $CH_2:CH:CH_2:CO_2H$, anethole, or antipyrine causes decolorisation (I solution is not decolorised), and the products are yellowish-red oils which could not be purified and contain I and S. $CHPh:CH:CO_2H$ and tiglic acid do not react. Addition of this solution to elaidic acid (I) in boiling C_6H_6 yields a mixture of *o*-iodo-*o*-thiocyanostearic acid (II) and *o*-dithiocyanostearic acid, the proportion of (I) being augmented by use of an excess of I in the reagent. (II) is transformed by $NaHCO_3$ in boiling $EtOH$ into *o*-thiocyanoelaidic acid, which could not be completely purified, and by KOH in boiling MeOH into *o*-ketostearic acid, m.p. 74—75°. Treatment of (II) with Zn dust in boiling AcOH affords nearly homogeneous (I). The products derived from oleic acid are similar to those derived from (II), but give stearic acid when reduced. Erucic acid yields *o*-iodo-*o*-thiocyanobehenic acid, whence non-homogeneous *o*-thiocyanoerucic acid and *o*-ketobehenic acid, m.p. 82—83° (Me ester, m.p. 57—58°). H. W.

Fats. XXXI. Diene synthesis with fats. III. Oiticica oil. H. P. KAUFMANN and J. BALTES (Ber., 1936, 69, [B], 2679—2683).— α -Licanic acid (I) is converted by maleic anhydride (II) in boiling C_6H_6 in absence of light into the adduct, $C_{22}H_{30}O_6$, m.p. 81—82°. β -Licanic acid, m.p. 97°, best obtained by the action of a trace of I on (I) or the total fatty acids of oiticica oil in Et_2O , does not give a readily purified adduct. Kaufmann's method is inapplicable to the determination of the I val. of (I), the observed vals. being particularly high if the solution is irradiated. CNS is added to 1 of the 3 double linkings of (I) and the diene no. corresponds with the addition of 1 mol. of (II). Bromination of the fatty acids after removal of (I) does not give a sparingly sol. hexabromide, thus proving the absence of linolenic acid, but a Br_4 -compound, m.p. 107—108°, is obtained. The oil contained (I) 70.0%, unsaturated non-conjugated acids 15.2%, saturated acids 9.9%, unsaponifiable matter 0.4%, and glyceryl residue 4.5%. H. W.

Wool fat. III. Lanopalmitic and lanoceric acid. T. KUWATA and Y. ISHII (J. Soc. Chem. Ind. Japan, 1936, 39, 358—359B).—Me lanopalmitate (I) with red P and boiling HI affords lanopalmitic acid, $C_{16}H_{32}O_2$, m.p. 42—43.5°, whereas with CrO_3 in Ac_2O at 50° followed by hydrolysis, lanopalminonic acid, m.p. 50—51.5° (monoxime), is formed, which indicates that (I) is a sec. alcohol. Hydrolysis of wool fat affords *K lanocerate*, converted by boiling conc. HCl into the lactide (II), $C_{64}H_{122}O_5$, m.p. 98.5—99°, of lanoceric acid. When heated at 400° with Se, (II) affords a substance, $C_{25}H_{40}$ or $C_{26}H_{52}$, b.p. 170—190°/5 mm. [picrate, m.p. 156—170° (decomp.)]. J. L. D.

Polymerisation of methyl esters of higher unsaturated acids. XVIII. Polymerisation products [obtained by heating] the methyl esters of linseed fatty acids. XIX. Increase in iodine value of the hydrogenated intermolecular polymerised ester. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 244—248, 249—251; cf. A., 1936, 705).—XVIII. If the Me esters of linseed fatty acids are heated at 280—290° in H_2 and then fractionated, all the fractions obtained give, when reheated, similar fractions, including one having b.p. <178°/3 mm. Fission of a C-C linking is indicated. With continued heating n and the I val. decrease.

XIX. The increase (on heating) in I val. of the esters of linseed and sardine oil acids decreases only very slightly after hydrogenation of the esters and is thus not due to absorption at conjugated linkings.

R. S. C.

Highly unsaturated acids in sardine oil. XII. Separation of octadecatrienoic acid $C_{18}H_{30}O_2$. XIII. Oxidation of methyl clupanodotate with potassium permanganate in acetone. XIV. Oxidation of potassium clupanodotate with potassium permanganate in aqueous solution. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1936, 11, 741—744, 745—750, 751—753; cf. A., 1935, 960).—XII. Fractionation of highly unsaturated acids by pptn. as Na salts from $COMe_2$ indicates the presence of a small proportion of octadecatrienoic acid, which was not characterised.

XIII. Oxidation of Me clupanodotate with $KMnO_4$ in $COMe_2$ affords $EtCO_2H$, $(-CH_2:CO_2H)_2$, Me H succinate, and AcOH, and confirms results obtained from O_3 on amyl clupanodotate (cf. A., 1935, 1482).

XIV. In agreement with the above, oxidation of K clupanodotate with $KMnO_4$ in KOH solution affords AcOH, $EtCO_2H$, and $(-CH_2:CO_2H)_2$. J. D. R.

α -Ethoxy-ethylenic acids. M. MEYER (Compt. rend., 1936, 203, 1074—1077).—Further examples of the reaction previously outlined (A., 1933, 491) are given: $CH_2:CH:CH_2Br \rightarrow Et \alpha$ -ethoxy- α -allylmalonate, b.p. 139°/15 mm., $\rightarrow \alpha$ -ethoxy- α -allylmalonic acid, m.p. 93°, $\rightarrow \alpha$ -ethoxy- α - Δ^7 -pentenoic acid, b.p. 120°/15 mm. (acid chloride, b.p. 56°/13 mm.; amide, m.p. 69.5°). $CHBu^{\delta}:CH:CH_2Br \rightarrow Et \alpha$ -ethoxy- α - ϵ' -methyl- Δ^8 -hexenylmalonate, b.p. 145°/4 mm., $Et \alpha$ -ethoxy- α - ϵ' -methyl- Δ^8 -hexenylmalonic acid $\rightarrow \alpha$ -ethoxy- ζ -methyl- Δ^7 -octenoic acid, b.p. 136°/3.5 mm. (acid chloride, b.p. 108°/14 mm.; amide, m.p. 56°). $CHPh:CH:CH_2Br \rightarrow Et \alpha$ -ethoxy- α -cinnamylmalonate, b.p. 183°/4 mm., \rightarrow

α -ethoxy- α -cinnamylmalonic acid, m.p. 130°, \rightarrow α -ethoxy- δ -phenyl- Δ^7 -pentenoic acid, b.p. 170°/3 mm. (acid chloride, b.p. 126—127°/3.5 mm.; amide, m.p. 98°). Undecenyl chloride (from undecenoic acid and SOCl_2 in NHMe_2), b.p. 120°/15 mm., \rightarrow Et α -ethoxy- α -undecenylmalonate, b.p. 150°/3 mm., \rightarrow α -ethoxy- α -undecenylmalonic acid, m.p. 56°, \rightarrow α -ethoxy- Δ^1 -tridecenoic acid, b.p. 170°/4 mm. (chloride, b.p. 136°/4 mm.; amide, m.p. 49°). F. N. W.

Highly unsaturated compounds. VI. Triene acid from pomegranate seeds. E. H. FARMER and F. A. VAN DEN HEUVEL (J.C.S., 1936, 1809—1811).—Evidence is given confirming Toyama and Tsuchiya's claim (A., 1935, 960) to have isolated an elaeostearic acid (punicic acid) differing from the α - and β -forms of the acid. F. N. W.

α -Ketol carboxylic acids. I. θ -Hydroxy- ι -keto- and ι -hydroxy- θ -keto-stearic acids. G. KING (J.C.S., 1936, 1788—1792).—Controlled oxidation (aq. KMnO_4 -KOH; 8—10 min.; 8—10°) of oleic acid affords 30—40% of a mixture of θ -hydroxy- ι - (I), m.p. 74° (semicarbazone, m.p. 152°; dinitrophenylosazone, m.p. 146.5°), and ι -hydroxy- θ -ketostearic acid (II), m.p. 75.5° (semicarbazone, m.p. 138.5°; dinitrophenylosazone, m.p. 146.5°), and 20—35% of dihydroxystearic acid (II). Elaidic acid similarly (but at 25°) affords 50—60% of (I) and (II) and 10—20% of (III). (I) or (II) on mild oxidation (AcOH-CrO_3 ; 24 hr.; room temp.) gives stearoxylic acid; stringent oxidation ($2\text{N-H}_2\text{SO}_4$ - KMnO_4 ; 10 min.; 100°) yields mainly nonoic (IV) and azelaic acids. Oxidation (HIO_4 ; 48 hr.; room temp.) of (I) affords (IV) and azelaaldehyde (2: 4-dinitrophenylhydrazones, m.p. 120°), whilst (II) gives nonaldehyde and azelaic acid. (I) on reduction (Zn-Cu; 48 hr.; 60—70°) yields (III), but (II) similarly treated is unaffected. Interconversion of (I) and (II) is complete in 24—36 hr. at room temp. or in 5 min. at 100°. F. N. W.

Hydrates of molecular compounds of zirconyl oxalate with oxalic acid and alkali oxalates.—See A., I, 93.

Chemical and biochemical dehydrogenation of $\alpha\alpha'$ -dideuterosuccinic acid. H. ERLÉNMEYER, W. SCHOENAUER, and H. SÜLLMANN (Helv. Chim. Acta, 1936, 19, 1376—1380).— $(\text{CHD}\cdot\text{CO}_2\text{Et})_2$ and SeO_2 give $\text{CO}_2\text{Et}\cdot\text{CD}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, H and D being removed with almost equal ease. $(\text{CHD}\cdot\text{CO}_2\text{H})_2$ (I) and succinodehydrazide give a $\text{CO}_2\text{H}\cdot\text{CD}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ with an increased D : H ratio; this is probably because this reaction is reversible and the D reacts more slowly. In conformity with this explanation (I) reacts more slowly than does $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ in Thunberg's dehydrogenation and Warburg's O_2 -consumption experiments. R. S. C.

Michael reaction with acetylenic esters. E. H. FARMER, S. C. GHOSAL, and G. A. R. KON (J.C.S., 1936, 1804—1809; cf. A., 1932, 1127).—Et phenylpropionate (I) with $\text{CHNa}(\text{CO}_2\text{Et})_2$ (II) affords a Na derivative, which with EtI (7 days; 100°) gives Et α -carbethoxy- β -phenyl- α -ethylglutaconate, b.p. 212—213°/10 mm., which on ozonolysis affords oxalic (III) and ethylmalonic acid. Similarly (I) with $\text{CMeNa}(\text{CO}_2\text{Et})_2$ (IV) yields a Na derivative, which with EtI gives Et α -carbethoxy- β -phenyl- α -methyl-

γ -ethylglutaconate, b.p. 211—213°/15 mm. (hydrolysed to β -phenyl- α -methyl- γ -ethylglutaconic acid, m.p. 75—76°; ozonised to EtCO_2H and Et benzylmethylmalonate), which with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ gives $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CPh}\cdot\text{CMe}(\text{CO}_2\text{Et})_2$ [ozonolysis products: (III), Et oxaloacetate, and Et benzoylmethylmalonate] and with NaOEt, Et α -carbethoxy- β -phenyl- α -methylglutaconate is formed. $(\text{C}\cdot\text{CO}_2\text{Et})_2$ (V) (modified prep.) with (IV) affords a Na derivative, which with EtI affords Et α -carbethoxy- α -methyl- γ -ethylglutaconate, b.p. 210—211°/20 mm. (ozonised to Et α -ketobutyrate and Et oxalylmethylmalonate), and with HCl gives Et α -carbethoxy- α -methylglutaconate (VI), b.p. 206—207°/20 mm. [ozonised to (III)], and Et oxalylmethylmalonate. (V) and (II) give a Na derivative (corresponding free ester, b.p. 204—205°/15 mm.), which with MeI (reflux in C_6H_6 ; 5 days) yields (VI). Et tetrolate with (IV) in presence of NaOEt [or with (II) followed by methylation] gives Et α -carbethoxy- $\alpha\beta$ -dimethylglutaconate, b.p. 170°/15 mm., which on ozonolysis affords Et acetylmethylmalonate (semicarbazone, m.p. 137°) and a compound, b.p. 110—130°/17 mm. Similarly Et propiolate affords a compound, b.p. 175°/20 mm., a compound, m.p. 134—135°, b.p. 22°/20 mm., and Et α -carbethoxy- α -methylglutaconate, which on ozonolysis gives (III) and Et formylmethylmalonate (?) (semicarbazone, m.p. 178°). (IV) with Et oxalochloride forms a compound, b.p. 173—175°/22 mm., which with $\text{NHPh}\cdot\text{NH}_2$ (1 mol.) affords $\text{NHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{CMe}(\text{CO}_2\text{Et})_2$, m.p. 120°, and with $\text{NHPh}\cdot\text{NH}_2$ (2 mol.) affords $\text{NHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CMe}(\text{CO}_2\text{Et})_2$, m.p. 275°. F. N. W.

Dihydroxystearic acid in castor oil. Y. TOYAMA and T. ISHIKAWA (Bull. Chem. Soc. Japan, 1936, 11, 735—741).—Me dihydroxystearate (I), m.p. 111—112°, slightly dextrorotatory in MeOH (diacetate, $[\alpha]_D^{20} +0.19^\circ$), obtained by "methanolysis" of castor oil, is hydrolysed to dihydroxystearic acid (II) (Et ester, m.p. 104—105°, and its diacetate, $[\alpha]_D^{20} +0.31^\circ$). (II) is oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ to n -nonoic and azelaic acid. (I) with HBr, followed by debromination with Zn and MeOH and hydrolysis, gives elaidic and oleic acids. (II) is thus d - θ - ι -dihydroxystearic acid. Attempts to resolve the racemic acid (from oxidation of oleic acid) failed. J. D. R.

Reaction mechanism of the electrolytic oxidation of tartaric acid. V. SIHVONEN (Suomen Kem., 1936, 9, B, 32; cf. this vol., 44; A., 1936, 54; 1933, 914).—The reaction mechanism is interpreted in the light of the results of other investigations. J. L. D.

Metallic complex salts of aliphatic polyhydroxy-compounds. W. TRAUBE and F. KUHBIER [with W. SCHRÖDER] (Ber., 1936, 69, [B], 2655—2663; cf. A., 1933, 1272).—Addition of aq. BaCl_2 to solutions of suitable quantities of tartaric acid, CuCl_2 , and NaOH gives the very sparingly sol. salts, $[\text{C}_4\text{H}_2\text{O}_6\text{Cu}]\text{Ba}_2\text{H}_2\text{O}$ and $[(\text{C}_4\text{H}_2\text{O}_6)_2\text{Cu}]\text{Ba}_2\cdot 3\text{H}_2\text{O}$. Gluconic acid (I), $\text{Cu}(\text{OH})_2$, and NaOH with BaCl_2 yield the compounds, $[\text{C}_6\text{H}_8\text{O}_7\text{Cu}]\text{Ba}_2\cdot 3\text{H}_2\text{O}$ and $[(\text{C}_6\text{H}_8\text{O}_7)_2\text{Cu}]\text{Ba}_2\cdot 9\text{H}_2\text{O}$; similar substances are derived from glucoheptonic acid. Mannitol (II),

$\text{Cu}(\text{OH})_2$, NaOH , and BaCl_2 yield the compound, $[\text{C}_6\text{H}_9\text{O}_6]_2\text{Cu}_2[\text{Ba}_2, 3\text{H}_2\text{O}]$; removal of mannitol is almost quant. if NaOH and BaCl_2 are replaced by $\text{Ba}(\text{OH})_2$. $[\text{C}_6\text{H}_{10}\text{O}_6\text{Cr}]K, 2\text{H}_2\text{O}$ is obtained from the Ba salt (*loc. cit.*) and KHSO_4 . Gradual addition of CrCl_3 and (I) in H_2O to 14.5% NaOH followed by BaCl_2 yields the salt, $[\text{C}_6\text{H}_7\text{O}_7\text{Cr}]K, 7\text{H}_2\text{O}$ (also anhyd.), whence $[\text{C}_6\text{H}_8\text{O}_7\text{Cr}]K, 2\text{H}_2\text{O}$; the complexes, $[\text{C}_6\text{H}_7\text{O}_7\text{Al}]K, 3\text{H}_2\text{O}$, (whence $[\text{C}_6\text{H}_8\text{O}_7\text{Al}]K, 2\text{H}_2\text{O}$) and $[\text{C}_6\text{H}_7\text{O}_7\text{Be}]K, 2\text{H}_2\text{O}$ (whence $[\text{C}_6\text{H}_8\text{O}_7\text{Be}]K, 2\text{H}_2\text{O}$) are obtained analogously. Similarly (II) gives the compound, $[\text{C}_6\text{H}_{10}\text{O}_6]_2\text{Bi}_2[\text{Ba}_2, 3\text{H}_2\text{O}]$. Quinic acid, $\text{Be}(\text{NO}_3)_3$, and NaOH followed by BaCl_2 yield the salt, $[\text{C}_{14}\text{H}_{17}\text{O}_{12}\text{Bi}]K, 7\text{H}_2\text{O}$. (II), Sb_2O_3 , and 7% $\text{Ba}(\text{OH})_2$ at 100° afford the complex, $[(\text{C}_6\text{H}_{12}\text{O}_6)_4\text{Sb}_2]K, 4\text{H}_2\text{O}$ or $[(\text{C}_6\text{H}_{12}\text{O}_6)_4\text{Sb}]K, 2\text{H}_2\text{O}$ if KOH replaces $\text{Ba}(\text{OH})_2$. (I) similarly yields the salt, $[\text{C}_6\text{H}_7\text{O}_7\text{Sb}]K, \text{H}_2\text{O}$, whence $[\text{C}_6\text{H}_8\text{O}_7\text{Sb}]K, \text{H}_2\text{O}$. Addition of SbCl_5 followed by BaCl_2 to (II) and 10% NaOH yields the substance, $[(\text{C}_6\text{H}_5\text{O}_7)_4\text{Sb}_2]K, 9\text{H}_2\text{O}$, whence $[(\text{C}_6\text{H}_8\text{O}_7)_4\text{Sb}_2]K, 9\text{H}_2\text{O}$. (I), $\text{Ni}(\text{NO}_3)_2$, and NaOH followed by BaCl_2 yield the compound, $[\text{C}_6\text{H}_8\text{O}_7\text{Ni}]K, 2\text{H}_2\text{O}$, whence $[\text{C}_6\text{H}_9\text{O}_7\text{Ni}]K$. With Na_2CO_3 and $\text{Co}(\text{NO}_3)_2$ or MnCl_2 (I) yields the complexes, $[\text{C}_6\text{H}_9\text{O}_7\text{Co}]Na$ and $[\text{C}_6\text{H}_9\text{O}_7\text{Mn}]Na$, respectively. Passage of air through a solution of (I), NaOH , and $\text{Co}(\text{NO}_3)_2$ in H_2O followed by addition of BaCl_2 yields the substance, $[\text{C}_6\text{H}_7\text{O}_7\text{Co}]K, \text{H}_2\text{O}$, whence $[\text{C}_6\text{H}_8\text{O}_7\text{Co}]K, \text{H}_2\text{O}$. The compound, $[\text{C}_6\text{H}_7\text{O}_7\text{Fe}]K, 3\text{H}_2\text{O}$, is transformed by (I) into the substance, $[\text{C}_{12}\text{H}_{19}\text{O}_{14}\text{Fe}]K, 2\text{H}_2\text{O}$. H. W.

Determination of ascorbic acid.—See A., III, 79.

Acetyl derivatives of monobasic sugar acid lactones. F. W. UPSON, J. M. BRACKENBURY, and C. LINN (J. Amer. Chem. Soc., 1936, 58, 2549—2552; cf. A., 1932, 43).—The $[\alpha]_D^{25}$ -time curves for the Ac derivatives of 10 γ - and 3 δ -lactones in $\text{COME}_2\text{-H}_2\text{O}$ (80:20) are very similar to those for the parent lactones in H_2O . 2:3:5:6-Tetra-acetyl- γ -D-galactono-, m.p. 67—68°, -d-gulono-, m.p. 103—104°, -d-talono-, and -l-rhamnono- and 2:3:4:6-tetra-acetyl- δ -l-rhamnono-, m.p. 71°, and -d-mannono-, m.p. 99—101°, -lactones are new. H. B.

Derivatives of l-allonic and l-altronic acid. I. F. L. HUMOLLER, W. F. McMANUS, and W. C. AUSTIN (J. Amer. Chem. Soc., 1936, 58, 2479—2481).—Rapid vac. evaporation of a freshly prepared aq. EtOH solution of l-allonic acid (phenylhydrazide, m.p. 142—145°, $[\alpha]_D -23.6^\circ$), dissolution of the residual syrup in EtOH, and re-evaporation gives δ -l-allonolactone (I), m.p. 140—144°, $[\alpha]_D -54.8^\circ \rightarrow +3.66^\circ$, which can be titrated against dil. bases (phenolphthalein) in cold aq. solution. (I) mutarotates more rapidly than γ -l-allonolactone (II), m.p. 129—130°, $[\alpha]_D +7.2^\circ \rightarrow +3.6^\circ$ (24 days) (A., 1934, 759). Fusion of (I) affords (II). A lactone could not be prepared from l-altronic acid, m.p. 110°, $[\alpha]_D -8.1^\circ$ (phenylhydrazide, m.p. 151—152°, $[\alpha]_D +18.4^\circ$) [from its Ca salt (*loc. cit.*) and $\text{H}_2\text{C}_2\text{O}_4$]. Oxidation of (II) with HNO_3 (d 1.15) give allomucic acid, m.p. 187.5° (decomp.) (inactive), which appears to differ from the acid obtained by $\text{C}_5\text{H}_5\text{N}$ -rearrangement (method: Fischer, A., 1891,

1193, 1444) of mucic acid (cf. Posternak, A., 1935, 846). All rotations are in H_2O at 20—25°. H. B.

Autoxidation of the complex metallic compounds of gluconic acid. W. TRAUBE and F. KUHBIER [with W. SCHRÖDER] (Ber., 1936, 69, [B], 2664—2666; cf. A., 1932, 362).—Autoxidation of the alkali Cu and Co complexes of gluconic acid occurs at $[\text{OH}']$ corresponding with that of Na_2CO_3 ; the amount of complex-united metal can be very greatly reduced, further for Cu than for Co. Similar experiments with the Ni and Mn complexes are recorded.

H. W.

Acetyl derivatives of gluconic and xylonic acids. R. T. MAJOR and E. W. COOK (J. Amer. Chem. Soc., 1936, 58, 2474—2477).—Acetylation ($\text{Ac}_2\text{O-ZnCl}_2$ at 0° —room temp.) of δ -gluconolactone followed by cold H_2O gives 2:3:4:6-tetra-acetyl-D-gluconic acid hydrate (I), m.p. 114—115°, $[\alpha]_D^{20} -5^\circ$ in EtOH (cf. Upson and Bartz, A., 1932, 43), also prepared by oxidation (Br-aq. KHCO_3) of glucose tetra-acetate (II). (I) is similarly further acetylated to penta-acetyl-D-gluconic acid ($+\text{H}_2\text{O}$), m.p. 72—73°, $[\alpha]_D^{20} +7.5^\circ$ in CHCl_3 , anhyd. m.p. 110—111°, $[\alpha]_D^{20} +11.5^\circ$ in CHCl_3 (Et ester, m.p. 103—104°, $[\alpha]_D^{20} +20.5^\circ$ in CHCl_3 ; phenylhydrazide, m.p. 152—154°, $[\alpha]_D^{20} +28^\circ$ in EtOH, obtained by similar acetylation of gluconphenylhydrazide), also prepared by oxidation (as above) of aldehydo-D-glucose penta-acetate. The semicarbazone from (II) is the ring-form (cf. Wolfrom *et al.*, A., 1934, 1092). Acetylation ($\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ at 60—70°) of D-xylosemicarbazone gives (mainly) the tetra-acetate, m.p. 232—233°, $[\alpha]_D^{20} +21^\circ$ in MeOH (ring structure); the residual product with HNO_2 affords aldehydo-D-xylose tetra-acetate (III). Successive treatment of the crude semicarbazone of l-xylose triacetate with $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$, $\text{MeOH-H}_2\text{C}_2\text{O}_4$, and HNO_2 gives aldehydo-l-xylose tetra-acetate (IV), m.p. 90—91°, $[\alpha]_D^{20} +22.5^\circ$ in CHCl_3 . Oxidation ($\text{Br-H}_2\text{O} + \text{CaCO}_3$) of (III), (IV), and the dl-compound, m.p. 85—86°, affords tetra-acetyl-D-, m.p. 86—88°, $[\alpha]_D^{20} +5^\circ$ in EtOH, -l-, m.p. 86—88°, $[\alpha]_D^{20} -4.5^\circ$ in EtOH, and -dl-, m.p. 134—135°, -xylonic acid, respectively. H. B.

Preparation and properties of penta-acetyl- α -keto-D-glucoheptonic acid. R. T. MAJOR and E. W. COOK (J. Amer. Chem. Soc., 1936, 58, 2477—2478).—Penta-acetyl-D-gluconyl chloride, m.p. 68—70°, $[\alpha]_D^{20} +2^\circ$ in CHCl_3 (from the anhyd. acid and PCl_5 in Et_2O ; SOCl_2 is unsatisfactory), with EtOH and $\text{Et}_2\text{O-NH}_3$ gives the Et ester and amide, respectively; with AgCN at 120—125° the nitrile (I), m.p. 116°, $[\alpha]_D^{20} +7^\circ$ in CHCl_3 , of penta-acetyl- α -keto-D-glucoheptonic acid, m.p. 160—161°, $[\alpha]_D^{20} \pm 0^\circ$ in EtOH (Et ester, m.p. 97—98°, $[\alpha]_D^{20} \pm 0^\circ$ in EtOH), results. (I) is hydrolysed by dioxan-HCl containing a little H_2O . Tetra-acetyl-Dl-xylonyl chloride, m.p. 90—92°, similarly gives Et tetra-acetyl-Dl-xylonate, m.p. 70—72°, tetra-acetyl-Dl-xylonamide, m.p. 130—132°, and tetra-acetyl- α -keto-Dl-gulononitrile, m.p. 125—126°. Acetylation ($\text{Ac}_2\text{O-ZnCl}_2$ at 0° —room temp.) of Me α -keto-D-gluconate affords a Ac_4 derivative, m.p. 168—169°, $[\alpha]_D^{20} -133^\circ$ in CHCl_3 (cf. Ohle and Wolter, A., 1930, 744). H. B.

Carbohydrate theory of origin of petroleum.

I. Conversion of acetaldehyde into hydrocarbons. N. A. ORLOV and E. M. TARASENKOVA (Ann. Leningrad State Univ., Chem. Ser., 1935, 1, 113—122).—Paracetaldehyde, H_2O , and CaO (300—330°; 3 hr.) yield tarry, liquid, and gaseous products. EtOH , HCO_2H , AcOH , EtCO_2H , and PrCO_2H were identified in the aq. layer, whilst the gas contained CO_2 62, C_nH_{2n} 2.14, CO 7.48, O_2 1.87, and H_2 25%. The tar was hydrogenated [MoS_3 and $\text{Al}(\text{OH})_3$ catalyst] at 370—380°/100 atm. (2 hr.), to yield liquid hydrocarbons, b.p. 34—150°, and a solid residue, which when oxidised gave BzOH and phthalic acid. The liquid product contained 70% of aromatic (C_6H_6 , PhMe , PhEt , xylene, C_{10}H_8 , 2- $\text{C}_{10}\text{H}_7\text{Me}$, and $\text{C}_{10}\text{H}_6\text{Me}_2$), 20% of naphthene, and 10% of paraffin hydrocarbons. R. T.

Depolymerisation of paraldehyde.—See A., I, 88.

Thermal decomposition of crotonaldehyde.

F. A. DELISLE, W. R. T. FOWLER, E. L. LOVELL, and W. URE (Trans. Roy. Soc. Canada, 1936, [iii], 30, III, 65—73).—The principal products of the thermal decomp. of crotonaldehyde between 430° and 482° and initial pressures from 25 mm. to 352 mm. are CO and propylene. CH_4 , H_2 , and O_2 are formed in small quantity. The reaction appears heterogeneous and approx. bimol. O. D. S.

Reaction of crotonaldehyde and amine salts.

C. MANNICH and K. ROTH (Arch. Pharm., 1936, 274, 527—537).— $\text{CHMe}:\text{CH}:\text{CHO}$ (I) and amine salts give complex mixtures of substances in dynamic equilibrium with each other. If piperidine is used under the simplest conditions (p_H 7.5, falling to 5 during the reaction), hydrogenation (PtO_2) of the reaction mixture gives 80% of 1-*n*-butylpiperidine (II), but this is of no constitutional significance, as it is formed also by hydrogenation of a mixture of PrCHO and piperidine. The crude reaction mixture of PrCHO and piperidine. The crude reaction mixture with Na-Hg and HCl gives amongst other products (II) (8%), γ -piperidino-*n*-butyl alcohol (III) (20%), and $\alpha\gamma$ -dipiperidino-*n*-butane (IV) (dibromobromide, m.p. 272—276°). (III) arises from β -piperidino-*n*-butaldehyde, the semicarbazone, m.p. 116—117°, of which is isolated in 20% yield from the crude reaction mixture; (IV) is formed from $\alpha\gamma$ -dipiperidino- Δ^2 -butene, which, however, partly decomposes into $\text{CHMe}:\text{C}:\text{CH}:\text{C}_5\text{H}_{10}\text{N}$, 10% of which is isolated from the crude reaction mixture. NHMe_2 leads similarly (Na-Hg) to $\text{NMe}_2\text{CHMe}:\text{CH}_2\text{CH}_2\text{OH}$; NH_2Me leads (Na-Hg) to much γ -methylamino-*n*-butyl alcohol (V), b.p. 81—82°/13 mm. (lit. 65°/14 mm.) [(*p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CO}$)₂ derivative, m.p. 132°], and some NHMeBu , b.p. 89—90° (picrate, m.p. 115°; platinichloride, m.p. 190°), and $\alpha\gamma$ -di(methylamino)butane, b.p. 157—158° [hydrochloride, hygroscopic, m.p. 186—187°; H_2 dioxalate, m.p. 190—190.5° (decomp.)]. (V) with 35% CH_2O or PhCHO (at 60—70°) gives 3:4-dimethyl-, b.p. 40—45°/20 mm. [hydrochloride, m.p. 175°; methiodide, m.p. 223—225° (decomp.)], and 2-phenyl-3:4-dimethyl-tetrahydro-1:3-oxazine, b.p. 131—135°/19 mm. (hydrochloride, m.p. 173—174°), respectively. R. S. C.

Condensation of β -cyclocitral with dimethylacetaldehyde. R. C. FUSON and R. E. CHRIST (Science, 1936, 84, 294—295).—The solution obtained by the action of $\text{Al}(\text{OPr}^i)_3$ on the crude reaction product of the condensation of β -cyclocitral with dimethylacetaldehyde gives a blue colour with SbCl_5 in CHCl_3 . The ultra-violet spectrum shows a max. at 328 μ . L. S. T.

Rapid approximate determination of acetone in aqueous solutions. E. K. NIKITIN (J. Appl. Chem. Russ., 1936, 9, 1543—1546).—1 ml. of 0.001—0.05% aq. COMe_2 and 1 ml. of 0.2% aq. furfuraldehyde are shaken with 1 ml. of 50% KOH , when the time elapsing before appearance of turbidity is a linear function of the COMe_2 content. Solutions containing >0.05% of COMe_2 should be diluted accordingly. R. T.

Pseudo-binary fusion diagram of monomeric and dimeric dihydroxyacetone.—See A., I, 82.

Condensation of ketones with formaldehyde in alkaline media. J. DESCOMBE (Compt. rend., 1936, 203, 1077—1079).—Condensation of the appropriate ketone in large excess with CH_2O in presence of K_2CO_3 affords γ -keto- β -methyl- β -hydroxymethyl-butyl alcohol, m.p. 66° (lit. 60°), b.p. 142—144°/14 mm. (diphenylurethane, m.p. 116°; oxime benzoate, m.p. 129°; acetobromohydrin, b.p. 106—107°/2 mm.), γ -keto- β -methyl- β -hydroxymethyl-*n*-amyl alcohol, m.p. 55°, b.p. 148—150°/16 mm. (diphenylurethane, m.p. 103—104°; acetobromohydrin, b.p. 140—143°/16 mm.), γ -keto- $\beta\beta$ -dimethylbutyl alcohol, b.p. 85—86°/16 mm. (oxime, m.p. 82°; *p*-nitrobenzoate, m.p. 82—83°), and γ -keto- $\beta\beta\delta$ -trimethyl-*n*-amyl alcohol, b.p. 97—98°/20 mm. (isooxazoline, m.p. 101—102°; *p*-nitrobenzoate, m.p. 82—83°). In addition COMePr^i also forms a compound, m.p. 58°. F. N. W.

Aliphatic and aliphatic-aromatic metalloketyls. I. B. NAZAROV (Ann. Leningrad State Univ., Chem. Ser., 1935, 1, 123—168).—Aliphatic ketones of the type COBu^iR react with Na in an inert atm. to yield intensely coloured Na ketyls, $\text{ONa}:\text{CBu}^i\text{R}$, which combine to afford Na-ethylene glycols of the type $(\text{ONa}:\text{CBu}^i\text{R})_2$. The intermediate ketyl has only an instantaneous existence when $\text{R} = \text{Me}$, Et , or Pr^i , and lasts only a few hr. or days when $\text{R} = \text{Pr}^i$, Bu^i , CHEt_2 , or CMe_2Et ; it is comparatively stable, existing in equilibrium with the glycols, when $\text{R} = \text{CMeEt}_2$ or CEt_3 . Ketones of type COPhR do not in any case behave analogously to those of the first group; those in which $\text{R} = \text{Me}$, Et , Pr^i , or Pr^i react similarly to those of the second, and in which $\text{R} = \text{CHEt}_2$, Bu^i , CMe_2Et , CMeEt_2 , or CEt_3 to those of the third, group. Na and COBu^i_2 (24 hr. at room temp., followed by 6 hr. at 100—120°) afford a product, which with aq. H_2SO_4 yields a mixture of CHBu^i_2OH and $\beta\beta\delta$ -tetramethyl- $\gamma\delta$ -ditert.-butylhexane- $\gamma\delta$ -diol, m.p. 85—86°, converted by conc. H_2SO_4 into Bu^i tritert.-butylmethyl ketone, b.p. 119—121°/12 mm. When dry CO_2 is passed through COBu^i_2 in Et_2O in presence of Na , and aq. H_2SO_4 is added to the reaction mixture, the products are COBu^i_2 and ditert.-butylglycollic acid, an oil. COMeBu^i and Na afford CHMeBu^iOH , pentamethyltert.-butylacetone (I), b.p. 200—209°, and

$\beta\gamma$ -ditert.-butyl- Δ^2 -buten- γ -ol, b.p. 105—107°/15 mm., converted by distillation from $\text{H}_2\text{C}_2\text{O}_4$ into (I) and $\beta\gamma$ -ditert.-butyl- Δ^2 -butadiene, b.p. 168—170°, which condenses with maleic anhydride in C_6H_6 to yield 4 : 5-ditert.-butyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride, m.p. 128—129°. (I) in EtOH and Na afford $\beta\beta\delta$ -trimethyl- δ -tert.-butylpentan- γ -ol, b.p. 99°/15 mm. (benzoate, m.p. 48—49°). COPr^{β}_2 and Na yield $\text{CHPr}^{\beta}_2\text{OH}$ and $\beta\epsilon$ -dimethyl- $\gamma\delta$ -diisopropylhexane- $\gamma\delta$ -diol, m.p. 90—91° (dibenzoate, b.p. 150—153°/19 mm.). COBu^{R} (R = Pr^{β} , CHEt_2 , CEt_3 , CMeEt_2 , CMe_2Et) and Na yield unstable pinacones, decomposed by aq. AcOH to give mixtures of the original ketones and their corresponding alcohols. COPhR (R = Pr^{β} , CHEt_2) and Na, followed by aq. acid, yield mixtures of the original ketones and their alcohols, whilst when R = Et or Pr^{α} $\gamma\delta$ -diphenylhexane- $\gamma\delta$ -diol, m.p. 130—133°, or $\delta\epsilon$ -diphenyloctane- $\delta\epsilon$ -diol, m.p. 94—96°, are obtained in addition. When R = Bu^{γ} , CMe_2Et , CMeEt_2 , or CEt_3 , the free Na ketyls are isolated; the second two react with H_2O to yield the original ketone and its alcohol, whilst the first two give, in addition, $\gamma\delta$ -diphenyl- $\beta\beta\epsilon\epsilon$ -tetramethylhexane- $\gamma\delta$ -diol, m.p. 127—130°, and $\delta\epsilon$ -diphenyl- $\gamma\gamma\zeta\zeta$ -tetramethyloctane- $\delta\epsilon$ -diol, m.p. 87—88°. $\text{CPhBu}^{\gamma}\text{ONa}$ and BzCl in Et_2O yield α -phenyl- α -benzoylpropyl alcohol, m.p. 68—70°. $\beta\beta$ -Dimethyl- $\delta\delta$ -diethylhexan- γ -ol, b.p. 225—228° (by reduction of the corresponding ketone), and $\text{H}_2\text{C}_2\text{O}_4$ (3 hr. at 140—200°) yield $\text{CHMe}:\text{CMe}_2$ (II), $\text{CHMe}:\text{CEt}_2$ (III) (nitrosochloride, m.p. 74°), and a mixture of $\text{C}_{12}\text{H}_{24}$ hydrocarbons, which were also the only products isolated from the dehydration products of $\text{OH}:\text{CHBu}^{\gamma}:\text{CMe}_2\text{Bu}^{\gamma}$. $\text{CMe}_2\text{Et}:\text{CHBu}^{\gamma}:\text{OH}$ when dehydrated by heating with 1 : 4- $\text{C}_{10}\text{H}_6\text{Br}:\text{SO}_3\text{H}$ at 180° affords $\text{CH}_2:\text{CMeEt}$, (II), $\text{CHEt}:\text{CMe}_2$ (IV), and decenes, whilst $\beta\beta\delta$ -trimethyl- δ -ethylhexan- γ -ol, b.p. 207—211°, gives (II), (III), (IV), and unidentified products of higher b.p. R. T.

Ketol condensation. T. VORTILA (Suomen Kem., 1936, 9, B, 30—32).— COMeEt and boiling COMe_2 during three weeks in presence of $\text{Ba}(\text{OH})_2$ afford ketols which are oxidised by I to mesityl oxide, β -methyl- Δ^2 -hexen- δ -one, and a compound, $\text{C}_8\text{H}_{12}\text{O}$, b.p. 147—149°/761 mm. (dinitrophenylhydrazone, m.p. 155—156° after sintering at 153°), derived from β -hydroxy- $\beta\gamma$ -dimethylpentan- δ -one (cf. A., 1929, 1273) are obtained. A probable mechanism is suggested. J. L. D.

(A) Interconversion of ketose and aldose sugars in dilute aqueous solution. H. R. GARBUTT and R. S. HUBBARD. (B) Changes in composition of dilute buffered carbohydrate solutions produced by boiling. R. S. HUBBARD and H. R. GARBUTT (Proc. Soc. Exp. Biol. Med., 1935, 33, 270—273, 274—279).—(A) When an aq. solution of glucose, fructose, or mannose is boiled, slow conversion of the sugar into a mixture of aldose and ketose forms takes place (4—6 hr.). O_2 has no effect on the reaction.

(B) Similar results are obtained in presence of OAc^{r} or PO_4^{r} buffers, the rate of conversion increasing with rise in p_{H} . In presence of PO_4^{r} buffer the loss in reducing power when O_2 is bubbled through the solution is more rapid than when OAc^{r} or no buffer at all is employed. W. O. K.

Asymmetric oxidation of sugars by optically active alkaline copper solutions. N. K. RICHTMYER and C. S. HUDSON (J. Amer. Chem. Soc., 1936, 58, 2540—2544; cf. A., 1935, 1355).—Oxidation of *d*- and *l*-altrose by alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ (prep. essentially that of Hanes, A., 1929, 478) and by Cu reagents prepared (method: Shaffer and Somogyi, A., 1933, 699) with *dl*- or *meso*-tartaric acid occurs to the same extent (for individual reagents). Cu reagents prepared with *d*- or *l*-tartaric acid oxidise the sugars asymmetrically, e.g., the *d*-sugar is oxidised to a greater extent by the *l*-reagent. The behaviour of *d*- and *l*-arabinose is strictly parallel. *d*-Glucose is, however, oxidised to approx. the same extent by all four Cu reagents. The relative reducing powers of 11 other sugars towards the *d*-, *l*-, and *dl*-reagents are compared. H. B.

Mechanism of carbohydrate oxidation. XXIII. Alkaline hydrolysis of oligosaccharides. H. GEHMAN, L. C. KREIDER, and W. L. EVANS (J. Amer. Chem. Soc., 1936, 58, 2388—2395).—Alkaline hydrolysis of oligosaccharides can occur if $\text{C}:\text{OR}$ (R is, e.g., glucosido) is present or if the original mol. can assume such a structure under the influence of the alkali. The disaccharides previously studied (A., 1930, 326; 1932, 148) give rise to intermediates which are then assumed to form glucosidic enediols; these are then hydrolysed to glucose [which can yield lactic acid (I)] and the enediol [triose converted into (I); tetroses converted into saccharinic acid (II)]. The yields of (I) obtained from gentiobiose (III) and glucosidodihydroxyacetone (IV) (as penta-acetate) with aq. KOH support the view that β -glucosidoglyceraldehyde is produced from (III). Comparison of (IV) with cellobiosidodihydroxyacetone (V) (as octa-acetate), (III) with gentiobiosidodihydroxyacetone (as octa-acetate), and cellobiose with (V) confirms the view (*loc. cit.*) that the hexosido-group of the 4-hexosidohexoses is the source of (I). The yields of (I) from the various oligosaccharides (A) investigated are < those from mixtures of the possible hydrolytic products except when $\text{CO}(\text{CH}_2\text{OH})_2$ is initially produced; these results are ascribed to slow degradation of (A) and/or to concurrent rearrangements leading to (II). The yields of (I) and (II) from a mixture of cellobiose octa-acetate and $\text{OH}:\text{CH}_2:\text{CO}:\text{CH}_2:\text{OAc}$ are compared. All experiments are carried out at 50° in N_2 . H. B.

Preparation of *d*-arabinose. C. NEUBERG and H. COLLATZ (Cellulosechem., 1936, 17, 128).—*d*-Arabonolactone in dil. aq. H_2SO_4 is reduced by Na-Hg to *d*-arabinose. A. G.

Heats of activation in the mutarotation of glucose.—See A., I, 89.

Preparation of aldehydo-sugar acetates. E. W. COOK and R. T. MAJOR (J. Amer. Chem. Soc., 1936, 58, 2410).—aldehydo-*d*-Glucose penta-acetate is obtained in nearly quant. yield by reduction (H_2 , Pd-BaSO₄, boiling xylene) of penta-acetyl-*d*-gluconyl chloride. H. B.

Structure of osazones and isolation of a new hexosazone anhydride. E. G. V. PERCIVAL (J.C.S., 1936, 1770—1774; cf. A., 1935, 1484).—Deacetylation [aq. NaOH (1.5%) in COMe_2 ; 24 hr.; room

temp.] of either glucosazone tetra-acetate or galactosazone tetra-acetate affords a *dianhydrohexosazone*, m.p. 238°, $[\alpha]_D^{20} - 88^\circ$ in COMe_2 [Ac_1 derivative, m.p. 135°, $[\alpha]_D + 108^\circ$ in CHCl_3 ; *Me*, ether, m.p. 172°, $[\alpha]_D^{20} - 170^\circ$ in CHCl_3 ; *dibromide*, m.p. 240° (decomp.)], a structure for which is proposed, involving the presence of a 2:6-oxide ring, a pyrazolidine and a pyrazoline ring, and the probable mechanism of its formation is discussed.

F. N. W.

Decomposition of *d*-fructose-6-phosphoric acid to *d*-arabonic acid-5-phosphoric acid and the enzymic scission of the latter. C. NEUBERG and H. COLLATZ (*Cellulosechem.*, 1936, 17, 125—128).—A 90% yield of *d*-arabonic acid-5-phosphoric acid (I) is obtained when *d*-fructose-6-phosphoric acid in aq. $\text{Ba}(\text{OH})_2$ is shaken with O_2 . The H_3PO_4 is split off from (I) by phosphatases.

A. G.

Micro-determination of maltose. S. M. STREPKOV (*Biochem. Z.*, 1936, 289, 38—40).—Maltose is oxidised by alkaline I to maltobionic acid, which on acid hydrolysis gives *d*-gluconic acid + glucose (I), the latter then being determined by the $\text{K}_3\text{Fe}(\text{CN})_6$ method. Any (I), mannose, galactose, or pentose in admixture with maltose is oxidised to the corresponding acid and during hydrolysis forms a non-reducing lactone. Any fructose present is partly oxidised by alkaline I and on hydrolysis is converted into laevulinic acid, whilst sucrose is first inverted by heating with acid before oxidation.

P. W. C.

Addition compounds of the carbohydrates.
III. Potassium hydroxide derivatives of cellobiose, lactose, and galactose. E. G. V. PERCIVAL and G. G. RITCHIE (*J.C.S.*, 1936, 1765—1770; cf. A., 1935, 964).—Cellobiose (I) (or its octa-acetate) with KOH in dry EtOH affords the compound (II), $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{KOH}$, which with Me_2SO_4 affords unchanged (I) and after acetylation β -methylcellobioside hepta-acetate with monomethylmethylcellobioside hexa-acetate from which, on hydrolysis followed by removal of glucose and treatment with $\text{NHPh} \cdot \text{NH}_2$, 6-methylglucosazone is obtained. In (II), therefore, one KOH is associated with the reducing group and the other with one of the primary alcohol groups. Similarly lactose forms the compound (III), $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{KOH}$, methylation of which followed by acetylation yields a non-reducing syrup from which by hydrolysis and acetylation 2:4-dimethylgalactose triacetate and 2-methylgalactose tetra-acetate are obtained, which after complete methylation are able to give tetramethylgalactopyranoseanilide, but no glucose derivatives. A structure is suggested for (III). Galactose penta-acetate similarly affords the compound, $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{KOH}$ [similar to the corresponding glucose compound (A., 1934, 1092)], which after methylation and subsequent acetylation gives a mixture of methylgalactoside α - and β -tetra-acetate.

F. N. W.

Rearrangement of sugar acetates by aluminium chloride. Cellobiose and its derivatives. N. K. RICHTMYER and C. S. HUDSON (*J. Amer. Chem. Soc.*, 1936, 58, 2534—2540).—Cellobiose octa-acetate and $\text{AlCl}_3 + \text{PCl}_5$ (2:1) in CHCl_3 give 40—45% of α -acetochlorocellobiose (I), m.p. 141—142°, $[\alpha]_D^{20} + 64.2^\circ$ in CHCl_3 (cf. A., 1926, 941), converted by

$\text{Ac}_2\text{O} \cdot \text{NaOAc}$ into *cellobiose α -octa-acetate* (II), two forms, m.p. 112°, resolidifying with m.p. 129—130°, and m.p. 129—130°, $[\alpha]_D^{20} + 48^\circ$ in CHCl_3 , which with AlCl_3 in CHCl_3 affords (I). (I) and Ag_2CO_3 in $\text{COMe}_2 + \text{a little H}_2\text{O}$ give *cellobiose α -hepta-acetate* (III), m.p. 130—131°, $[\alpha]_D$ (in CHCl_3) $+ 22.3^\circ \rightarrow + 15.1^\circ$ (5 days) $+ 2\text{Et}_2\text{O}$, m.p. 60° (decomp.), resolidifying with m.p. 130—131°, β -hepta-acetate ($+ \text{Et}_2\text{O}$) (IV), m.p. 80° (decomp.), $[\alpha]_D$ (in CHCl_3) $+ 3.9^\circ \rightarrow + 15.1^\circ$ (7 days; on Et_2O -free basis) (main product), and a little of a β -hepta-acetate (V) (ortho structure), m.p. 216°, $[\alpha]_D + 1^\circ$ in CHCl_3 (no mutarotation). Acetylation ($\text{Ac}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$ at -10° to room temp.) of (IV) and (V) gives (mainly) *cellobiose β -octa-acetate* (VI), 2 forms, m.p. 103—105° and 113—114°, $[\alpha]_D^{20} - 13^\circ$ in CHCl_3 (hydrate, m.p. 87—93°), which forms a 1:2 compound ($+ 3\text{Et}_2\text{O}$), m.p. 70° (decomp.), $[\alpha]_D + 25.8^\circ$ in CHCl_3 , m.p. (Et_2O -free) 70—85°, with (II). (III) is similarly acetylated to (mainly) (II). De-acetylation [$\text{MeOH} \cdot \text{Ba}(\text{OMe})_2$] of (II)—(VI) affords *cellobiose* ($+ \text{H}_2\text{O}$) (VII), m.p. 148° (decomp.) (softens at 133°), $[\alpha]_D + 13.6^\circ$ in H_2O , which is the β -form since cautious acetylation gives 85% of (VI). Hydrolysis (N-HCl) of (VII) affords *d*-glucose and *d*-altrose, whilst oxidation (method: A., 1929, 1043) followed by hydrolysis ($\text{N-H}_2\text{SO}_4$) yields *d*-glucose and *d*-altronic acid (VIII). (VII) is thus 4- β -*d*-glucosido-*d*-altrose. Preliminary work has shown that the Ca salt ($+ 3.5\text{H}_2\text{O}$) of (VIII) is a convenient substance for the prep. (by degradation) of *d*-ribose.

H. B.

Enzymic hydrolysis of β -glucosides of tertiary alcohols.—See A., III, 30.

Colour reactions for cardiac glucosides. Digitoxin, strophanthin-K, ouabain, and Digitalis verum. J. A. SANCHEZ (*J. Pharm. Chim.*, 1936, [viii], 24, 549—558).—Digitoxin (I), strophanthin-K (II), and ouabain (III) in AcOH give with a 0.3% solution of vanillin in conc. HCl at 100°, indigo-blue, deep blue, and violet colours, respectively. Evaporation of a solution of 0.1% $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ (in 20 c.c. of EtOH and 14 drops of conc. H_2SO_4) with D. verum (IV) and digitonin (V) at 100° and dissolution in AcOH give deep eosin-red solutions, whereas (I), (II), and (III) do not. With a solution of one drop of $\text{Br} \cdot \text{H}_2\text{O}$ in 20 c.c. of H_2SO_4 (IV) and (V) give a cerise and no colour, respectively. Modifications for application to pharmacological preps. are given.

R. F. P.

Size of polysaccharide molecules. W. N. HAWORTH (*Monatsh.*, 1936, 69, 314—318).—Evidence is adduced that under various conditions starch can be acetylated without appreciable rise in the reducing power. The acetates can possess all degrees of viscosity. By direct methylation without passing through the acetate, or by methylation of the above acetates, derivatives of varying degrees of viscosity can be obtained. It appears that there is no relationship between viscosity and observed chemical chain length, which remains invariable for specimens of undegraded starch derivatives. When hydrolytic degradation of starch into dextrins is attempted the val. for the chemical assay of the end group diminishes progressively. The chemical end group method of assay indicates the presence of 12 or 18 glucose units in glycogen from rabbit liver, fish liver, and fish

muscle. Similar results are given by viscosity measurements using the Staudinger formula, but osmotic pressure measurements with a Cellophane membrane indicate a much larger particle size. Chemical assay of methylated inulin indicates a chain of about 30 fructose units, confirmed by determination of the osmotic pressure. Viscosity measurements, using Staudinger's factor for cellulose, show the presence of only 9 fructose units. In any comparison of the mol. wt. of various polysaccharides it is necessary to recognise that aggregation may be caused by lengthening of the chain and also by lateral combination between chains. Thus the chemical unit of methylated xylan is composed of about 18 pentose residues, whilst physical evidence suggests that ≤ 4 of these chains are grouped together by co-ordination or other type of union between the reducing end of the chain and an intermediate OH position of an adjoining chain.

H. W.

Mol. wt. of inulin. B. B. WESTFALL and E. M. LANDIS (J. Biol. Chem., 1936, **116**, 727—734).—The mol. wt. of inulin was determined by a thermoelectric v.-p. technique (cf. Baldes, A., 1934, 986). That of the purest sample averaged 5100. E. A. H. R.

Micro-determination of inulin. S. M. STREPKOV (Biochem. Z., 1936, 288, 301—302).—The application of the phosphomolybdic acid method of Stöhr (A., 1934, 315) for fructose is described. F. O. H.

Acetylation and methylation of cellulose. **Constitution of carbohydrates.** P. KARRER and E. ESCHER (Helv. Chim. Acta, 1936, **19**, 1192—1198).—Methylation of cellulose which has not been degraded ceases at 42.2% OMe in the product, which contains no free OH ($\text{Ac}_2\text{O}-\text{C}_5\text{H}_8\text{N}$; Zerevitinov) and yields some 2 : 3-dimethylmethylglucoside (isolated as di-*p*-toluenesulphonate) when hydrolysed. The unreactive OH may be at 2 or 6 and may be sterically hindered or bound in anhydride linkings. There is one unreactive OH for each 4—5 C_6 units. The completely symmetrical formula for cellulose (and other polysaccharides) is thus in doubt. R. S. C.

Syntheses from ethanolamine. III. Synthesis of ethyl *N*-β-chloroethylcarbamate and β-chloroethylcarbimide. H. WENKER (J. Amer. Chem. Soc., 1936, 58, 2608).— $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ (I) and SOCl_2 afford Et *N*-β-chloroethylcarbamate, b.p. 128—130°/13 mm., converted [as is (I)] by PCl_5 into β-chloroethylcarbimide, b.p. 135°, which with NH_2Ph and *p*-OEt-C₆H₄-NH₂ gives *N*-phenyl-, m.p. 124°, and *N-p*-phenetyl-, m.p. 149°, -*N'*-β-chloroethylcarbimide, respectively. H. B.

Betaine aurichloride. M. BECKER (Biochem. Z., 1936, 288, 348—350).—The betaine (B) aurichlorides of Fischer (A., 1902, i, 428) and Willstätter (*ibid.*, 661) were not as described ($\text{HBAuCl}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ and $\text{HBAuCl}_4 \cdot 2\text{H}_2\text{O}$, respectively), but basic compounds with $\text{B} : \text{AuCl}_3 = >1 : 1$ mol. The formation of such compounds is avoided by the use of excess of AuCl_3 in N-HCl . F. O. H.

Synthesis of serine. L. R. SCHILTZ and H. E. CARTER (J. Biol. Chem., 1936, **116**, 793—797).—60% $\text{CH}_2\text{:CH}\cdot\text{CO}_2\text{Me}$ in MeOH with $\text{Hg}(\text{OAc})_2$ gives $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Me})\cdot\text{Hg}\cdot\text{OAc}$, converted by aq. KBr 2^{**} (A., II.)

into the corresponding mercuribromide, which with Br-CHCl_3 (sunlight) yields *Me* α -bromo- β -methoxypropionate, b.p. $70-80^\circ/6$ mm., hydrolysed by 0.5*N*-NaOH at room temp. to the corresponding acid, b.p. $91^\circ/2$ mm. This with conc. aq. NH_3 at $80-90^\circ$ affords the α - NH_2 -acid, m.p. $200-210^\circ$ (decomp.) (*Bz*, m.p. $147-148^\circ$, and formyl derivative, m.p. $151-152^\circ$), demethylated by HBr to serine (31-39% over-all yield). J. W. B.

Multivalent amino-acids and peptides. VII.
Derivatives of *dl*- α -aminotricarballylic acid.
J. P. GREENSTEIN (*J. Biol. Chem.*, 1936, **116**, 463—467).— α -Aminotricarballylic acid (I) is converted by cold AgNO_2 -*N*-HCl into *dl*-isocitric acid, isolated as its Ba salt and converted into its lactone, m.p. 153°. (I) with HCl-MeOH affords its $\beta\gamma$ - Me_2 ester, m.p. 165°, converted by 28% aq. NH_3 into the NH_4 salt, m.p. 214°, of 4-carboxylamidopyrrolidone-5-carboxylic acid, m.p. 178°, which is obtained by the action of H_2S on the Ag salt. J. W. B.

Synthesis of glutathione. V. DU VIGNEAUD and G. L. MILLER (J. Biol. Chem., 1936, **116**, 469—476).— α -Benzylcysteinylglycine (A., 1935, 1486) is converted by HCl-MeOH at $<0^\circ$ into its *Me ester hydrochloride*, from which the free *Me ester* (I) is liberated with $\text{NH}_4\text{Et}_2\text{-CHCl}_3$. α -Me *N*-carbobenzyl-oxyglutamate (Harington *et al.*, A., 1935, 1110) with PCl_5 in Et_2O at 0° affords its γ -chloride, excess of which is condensed with (I) in CHCl_3 , cooled in solid CO_2 , to give the *Me ester of α -methyl-*N*-carbobenzyl-oxy- γ -glutamyl-*S*-benzylcysteinylglycine* (II), which is obtained (73% yield) by hydrolysis using Harington's method (*loc. cit.*). Reduction of (II) with Na-liquid NH_3 affords glutathione (27% yield), isolated and purified through its Hg and Cu salts. J. W. B.

Formation of taurine by decarboxylation of cysteic acid. A. WHITE and J. B. FISHMAN (J. Biol. Chem., 1936, **116**, 457—461).—Decarboxylation of cysteic acid (from *l*-cystine) to taurine, m.p. 327—328° (decomp.) (corr.) (Friedmann, A., 1903, i, 75), occurs only within a limited temp. range and was always successful at 235—240°. J. W. B.

Formation of lactams from lactones. E. SPATH and J. LINTNER (Ber., 1936, 69, [B], 2727—2731).—Lactones appear to be convertible into lactams by NH_3 , primary aliphatic, fatty-aromatic, or aromatic amines if the reaction partners can withstand the requisite temp. Lactones derived from OH-acids with phenolic OH form a present exception. Butyrolactone (I) and NH_3 in absence of solvent at 200° afford pyrrolidone, m.p. $23\text{--}24^\circ$, in 64% yield. Similarly, 5-methylpyrrolid-2-one, m.p. $43\text{--}44^\circ$, is obtained from γ -valerolactone and $\text{ZnCl}_2 \cdot 6\text{NH}_3$ at $220\text{--}230^\circ$. (I) and NH_2Me at 200° yield γ -hydroxybutyrmethylamide, b.p. $125\text{--}130^\circ$ (bath)/1 mm., whereas at 280° the product appears to be 1-methylpyrrolid-2-one. Under like conditions (I) and allylamine afford γ -hydroxybutyrallylamide, m.p. $27\text{--}27.5^\circ$, and 1-allylpyrrolid-2-one, b.p. $115\text{--}120^\circ$ (bath)/12 mm. (hydrochloride), whilst (I) and $\text{CH}_2\text{Ph} \cdot \text{NH}_2$ give γ -hydroxybutylbenzylamide, m.p. $74\text{--}75^\circ$, and non-cryst. 1-benzylpyrrolid-2-one, b.p. $130\text{--}140^\circ$ (bath)/1 mm. 1-Phenyl-, m.p. $68\text{--}69^\circ$, and 1-*p*-tolyl-, m.p.

81—82°, -pyrrolid-2-one are obtained from (I) and NH_2Ph or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ at 215° and 210—220°, respectively. H. W.

NN'-Dimethyldiamide of tartaric acid and the NN'-dinitrodimehyldiamide of tartaric acid dinitrate. T. URBAŃSKI (Rocz. Chem., 1936, 16, 334—338).—The velocity of reaction between NH_2Me and esters of tartaric acid, and the yield of NN'-dimethyldiamide (I) of tartaric acid, m.p. 213—214° (lit., 189°), fall in the series $\text{Me} > \text{Et} > \text{Pr}^a$ tartrate. Tartaric acid dinitrate NN'-dinitrodimehyldiamide (II), m.p. 114° (decomp.), is obtained by adding 60 g. of Ac_2O to 10 g. of (I) in 180 g. of HNO_3 , at $\approx -2^\circ$. (II) is readily detonated by shock or heat, and yields gels with cellulose nitrate. R. T.

Determination of allylthiocarbimide in air. M. S. GERSCHENOVITSCH, R. S. BELOVA, and I. A. SAMARTZEVA (J. Appl. Chem. Russ., 1936, 9, 1547—1549).—The air is aspirated at the rate of 7 litres per hr. through three wash-bottles containing 95% EtOH at 40—45°, 25 ml. of 0.1N- AgNO_3 and 5 ml. of 10% aq. NH_3 are added, the solution is heated to 80° and filtered, and residual Ag is determined by the Volhard method. R. T.

Andrussov's theory of the catalytic preparation of hydrocyanic acid.—See A., I, 90.

Preparation of zinc and cadmium cyanides.—See A., I, 92.

Synthesis of azido-derivatives of acetylenic hydrocarbons. Synthesis of $\text{CH}_3\text{C}[\text{CH}_2]_8\text{CH}_3\cdot\text{N}_3$. A. P. OSKERKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 415—436).—The reduction of $\text{CH}_3\text{C}[\text{CH}_2]_8\text{CO}_2\text{Et}$ by Na in anhyd. MeOH, EtOH, or Bu^nOH gives Δ^8 -undecinen- α -ol, m.p. $>4^\circ$, b.p. 108—109°/2 mm. (phenylurethane, m.p. 51°; acetate, b.p. 114—115°/4 mm.), which adds Br_2 and is converted by AgNO_3 into the salt, $\text{AgNO}_3\cdot\text{C}_{11}\text{H}_{19}\text{OAg}$, and by PBr_3 in α -bromo- Δ^8 -undecinen- α -ol (I), b.p. 98—99°/2 mm. Interaction of (I) and NaN_3 in aq. COME_2 yields α -azido- Δ^8 -undecinen- α -ol, a liquid, which adds Br_2 , evolves with conc. H_2SO_4 2 atoms of N, and is converted by AgNO_3 into the compound, $\text{AgNO}_3\cdot\text{C}_{11}\text{H}_{18}\text{N}_3\text{Ag}$. J. J. B.

Chloride of allylphosphorous acid, and certain of its reactions. V. M. PLETZ (J. Gen. Chem. Russ., 1936, 6, 1198—1202).— $\text{PCl}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ (I) yields $\text{CH}_2\text{CH}:\text{CH}_2\text{Br}$ and POCl_2Br with Br in CCl_4 , and allylthiophosphoric dichloride, b.p. 74°/25 mm., when heated with S in CS_2 . (I) and MgEtI or Mg allyl iodide in Et_2O afford $\text{CH}_2\text{CH}:\text{CH}_2\text{I}$ and ethyl- or allyl-phosphinic acid, decomp. 120°. R. T.

Constitution of complex metallic salts. V.—See A., I, 15.

Introduction of silicon into fats. H. P. KAUFMANN (Ber., 1936, 69, [B], 2685).—A comment on the communication of Klein *et al.* (A., 1936, 1368). H. W.

Complex compounds of mercury and copper halides with aliphatic amines.—See A., I, 92.

Complex compounds with two co-ordination shells from hexamminechromic and triethylene-diaminechromic ions.—See A., I, 94.

Stereochemistry of co-ordinative quadrivalent nickel.—See A., I, 15.

Dipole measurements of isomeric plato-complexes.—See A., I, 14.

Isomerism of ethylene compounds of platinum. I. I. TSCHERNIAEV and A. D. GELMAN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 181—184).—By treating K_2PtCl_4 first with C_2H_4 and then with NH_3 or $\text{C}_5\text{H}_5\text{N}$ (B), *trans*- $[\text{C}_2\text{H}_4\text{BPtCl}_2]$ is formed, contrary to the Peyronnet rule. A *cis*-compound was obtained by passing C_2H_4 through a solution of a $\text{M}[\text{NH}_3\text{PtCl}_2]$ (M = metal). These results are ascribed to the great *trans*-influence of C_2H_4 . R. C. M.

Dehydrogenation of cyclohexane catalysed by chromic oxide.—See A., I, 90.

Phenylcyclopentylmethane and cyclopentylcyclohexylmethane in relation to catalytic hydrogenation. J. I. DENISENKO (J. Gen. Chem. Russ., 1936, 6, 1263—1266).— CH_2PhCl , cyclopentanone, and Mg in Et_2O yield 1-benzylcyclopentan-1-ol, b.p. 129—130°/11 mm., converted by heating with anhyd. $\text{H}_2\text{C}_2\text{O}_4$ into 1-benzyl- Δ^1 -cyclopentene, b.p. 120—122°/10 mm., and this gives benzylcyclopentane (I), b.p. 234—236°/750 mm., when hydrogenated (Pt black-EtOH). (I) yields cyclopentylcyclohexylmethane (II), b.p. 224—226°/750 mm., when passed with H_2 over Pt-C catalyst at 196—200°, and both (I) and (II) give chiefly *n*-hexylbenzene and H_2 when passed over the same catalyst at 300—310°. R. T.

Photo-oxidation of carotene. E. BAUR [with P. E. CHRÉTIEN] (Helv. Chim. Acta, 1936, 19, 1210—1212).—Ultra-violet irradiation of α -carotene in CHCl_3 causes an initial, rapid, autocatalysed absorption of O_2 with deepening of colour, followed by a slow further absorption, independent of light and causing loss of colour. The first step is reversible; its inception and extent depend on the O_2 pressure, and irradiation in vac. after completion of the first step causes evolution of O_2 . R. S. C.

Reactivity of aromatic chloro-derivatives. Action of certain amines on halogens substituted in the nucleus. A. MARGINKÓW and E. PĘŻĄEK (Rocz. Chem., 1936, 16, 395—402).—The reactivity of aq. amines with aromatic halogen derivatives \propto the dissociation const. of the amino, and rises in the series $\text{NH}_3 < \text{NH}_2\text{Me} < \text{NHMe}_2$. In the case of higher amines (NH_2Et , NHMeEt , NH_2Bu^n , NHMeBu^n , and mono- and di-isoamylamine) the reactivity is determined by other factors, and falls with increasing mol. wt. R. T.

Pyrogenic decomposition of aliphatic-aromatic hydrocarbons. A. DOBRJANSKI (Ann. Leningrad State Univ., Chem. Ser., 1935, 1, 105—112).—When heated at 600—650° PhMe and xylene remain unchanged, PhEt gives C_6H_6 , PhMe, and $\text{CHPh}\cdot\text{CH}_2$, (I) in approx. equal amounts, PhPr ^{α} , PhBu ^{β} , and isoamylbenzene yield chiefly PhMe, PhPr ^{β} chiefly (I), with C_6H_6 and PhMe as admixtures, PhBu ^{α} and *n*-amylbenzene afford chiefly (I) and PhMe, and PhBu ^{γ} gives chiefly C_6H_6 . It is concluded that the products of pyrolysis are PhMe, (I), or C_6H_6 , according to whether the Ph is combined with a primary, sec., or tert. C. R. T.

Constitution of the two *tert*.-butyl-*p*-cymenes. H. BARBIER (Helv. Chim. Acta, 1936, 19, 1345—1354).—The orientations of the hydrocarbons obtained by butylation of *p*-cymene and that of certain NO_2 -derivatives are established. The product (I), m.p. 132° , of musk-like odour is 2 : 6-dinitro-3-*tert*.-butyl-*p*-cymene ($\text{Me} = 1$). Crude *tert*.-butyl-*p*-cymene (II) and 70% HNO_3 at $0-5^\circ$ give a nitro-3-*tert*.-butyl-*p*-cymene, m.p. 62° , b.p. $125^\circ/2-3$ mm., volatile in steam, reduced by SnCl_2 to the NH_2 -compound, m.p. 76° , which yields ($\text{HNO}_2\text{-SnCl}_2$) pure 3-*tert*.-butyl-*p*-cymene (III), b.p. $226^\circ/729$ mm. (III) with CrOCl_2 gives 4-isopropyl-3-*tert*.-butylbenzaldehyde, b.p. $101^\circ/2-3$ mm., m.p. 43° (semicarbazone, m.p. 222°), oxidised by 20% HNO_3 to 4-isopropyl-3-*tert*.-butylbenzoic acid, m.p. 187° , which, when distilled with NaOEt at $2-3$ mm., gives o-isopropyl-*tert*.-butylbenzene, b.p. $208^\circ/729$ mm. [$(\text{NO}_2)_2$ -derivative, m.p. 142° , obtained by HNO_3 ($d\ 1.5$)], stable to oxidation by HNO_3 . PhBu^r , Pr^iCl , and AlCl_3 give *m*-isopropyl-*tert*.-butylbenzene, b.p. $216^\circ/729$ mm. [$(\text{NO}_2)_2$ -derivative, m.p. 149°], oxidised by hot 20% HNO_3 to *m*- $\text{C}_6\text{H}_4\text{Bu}^r\text{CO}_2\text{H}$. *p*- $\text{C}_6\text{H}_4\text{Pr}^i\text{Bu}^r$ (obtained from PhPr^i , Bu^rOH , and conc. H_2SO_4 at -5°), b.p. $222^\circ/729$ mm., with 20% HNO_3 gives *p*- $\text{C}_6\text{H}_4\text{Bu}^r\text{CO}_2\text{H}$, but is resinified by HNO_3 ($d\ 1.5$). Menthone does not react with MgBu^rCl , but pure carvone gives a fair yield of 2-methyl-3-*tert*.-butyl-5-isopropenylcyclohexanone (cf. lit.), b.p. $103^\circ/2-3$ mm. (semicarbazone, m.p. 62°), resinified by Na-EtOH , but smoothly hydrogenated (Ni) to 6-*tert*.-butyltetrahydrocarveol ($\text{Me} = 1$), b.p. $203-206^\circ/2-3$ mm., which by dehydration (ZnCl_2) and dehydrogenation (S) yields the 2-*tert*.-butyl-*p*-cymene, b.p. 237° , contained in small amounts in (II). The $(\text{NO}_2)_2$ -derivative, m.p. 141° , obtained from (II), with phenanthraquinone gives a quinoxaline derivative, m.p. $191-192^\circ$, and is thus the 5 : 6- $(\text{NO}_2)_2$ -compound; the other, (I), does not react. R. S. C.

Thermal polymerisation of pure styrene.—See A., I, 86.

Mechanism of addition of hydrogen and bromine to ω -nitrostyrenes and α -nitrostilbenes. B. REICHERT (Arch. Pharm., 1936, 274, 505—519).—The addition of H_2 to ω -nitrostyrenes and α -nitrostilbenes is greatly influenced by the formation of mol. compounds with the solvent (evidenced by bathochromy). $\text{C}_5\text{H}_5\text{N}$ adds to the O of the *aci*-form, acid to the O of the NO_2 -form. The following reactions occur: (a) $\text{CHAr}:\text{C}:\text{N}(\text{OH})\text{O}\cdots\text{C}_5\text{H}_5\text{N}$ (I) \rightarrow $\text{CHAr}:\text{CH}:\text{NH}(\text{OH})\text{O}\cdots\text{C}_5\text{H}_5\text{N} \rightarrow \text{CH}_2\text{Ar}:\text{CH}:\text{NH}(\text{OH})_2 \rightarrow \text{CH}_2\text{Ar}:\text{CH}:\text{N}:\text{OH}$ (II), the $\text{C}_5\text{H}_5\text{N}$ then acting as partial poison to the catalyst and preventing further reduction to the amine; (b) (I) $\rightarrow -\text{CHAr}:\text{CH}:\text{NO}:\text{OH} \rightarrow (\cdot\text{CHAr}:\text{CH}_2:\text{NO}_2)_2$; (c) $\text{CHAr}:\text{CH}:\text{NO}:\text{O}\cdots\text{H}_2\text{SO}_4 \rightarrow \text{CH}_2\text{Ar}:\text{CH}:\text{N}(\text{OH})\text{O}\cdots\text{H}_2\text{SO}_4 \rightarrow \text{CH}_2\text{Ar}:\text{CH}_2:\text{NH}(\text{OH})\text{O}\cdots\text{H}_2\text{SO}_4 \rightarrow \text{CH}_2\text{Ar}:\text{CH}_2:\text{NO}$ [= (I)], further reduction to the amine occurring in presence of acid, e.g., H_2SO_4 ; reduction to the amine does not occur in HCl-EtOH , as the HCl is destroyed during the first stages of reduction. Reactions (a) and (b) always occur simultaneously, but to extents which vary according to the conditions.

Reduction of α -nitrostilbenes proceeds analogously. α -Nitrostilbene and Br at 100° give a dibromide, m.p. 119° , which can be crystallised from ligroin, but loses 2 Br in hot EtOH or COMe_2 or cold $\text{C}_5\text{H}_5\text{N}$, and resists attempts to remove HBr. 3 : 4 : 5- $(\text{NO}_2)_3\text{C}_6\text{H}_2:\text{CH}:\text{CH}:\text{NO}_2$ gives $(\text{H}_2\text{-Pd-C; C}_5\text{H}_5\text{N})$ 3 : 4 : 5-trimethoxyphenylacetaldoxime, m.p. $82-83^\circ$, further hydrogenated (PtO_2) in $\text{EtOH-H}_2\text{C}_2\text{O}_4$ at 50° to mescaline and di-(3 : 4 : 5-trimethoxyphenylethyl)amine (hydrochloride, m.p. 229°). β -Nitro-3 : 4-methylenedioxy stilbene and $\text{H}_2\text{-PtO}_2$ in $\text{AcOH-H}_2\text{SO}_4$ give the corresponding saturated base. R. S. C.

Derivatives of 4-cyclohexyldiphenyl. F. R. BASFORD (J.C.S., 1936, 1780—1781).—4'-Bromo-4-cyclohexyldiphenyl (I), m.p. 154° , is obtained by the interaction of 4-bromodiphenyl and cyclohexyl bromide in presence of AlCl_3 (6 hr. at 18° followed by 15 min. at 40°) or by the addition of Br to 4-cyclohexyldiphenyl (II) in AcOH containing NaOAc (10 min.; 120°). Oxidation ($\text{AcOH-Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$) of (I) (90 min.; 95°) affords *p*- $\text{C}_6\text{H}_4\text{Br-CO}_2\text{H}$, whilst Se dehydrogenation (30 min.; $330-360^\circ$) gives *p*- $\text{C}_6\text{H}_4\text{Ph}_2$. (I) with Br (15 min.; 160° followed by 15 min.; 200°) yields *p*- $\text{C}_6\text{H}_4\text{Br-C}_6\text{H}_4\text{Ph-p'}$ (III). 4'-Bromo-4-(tribromocyclohexyl)diphenyl, m.p. 148° , which on thermal decomp. at $160-220^\circ$ affords (III) with loss of HBr, is obtained by the addition of Br to (II) (24 hr.; 18°) or to (I) (2 hr.; room temp. finished at 50° ; Fe catalyst). F. N. W.

Synthesis of alkylated polycyclic aromatic hydrocarbons. M. LERER (Ann. Office nat. Combust. liq., 1935, 10, 455—464; Chem. Zentr., 1936, i, 1422).—In the presence of alkyl halides, Na reacts with otherwise unreactive hydrocarbons; the reaction is probably between hydrocarbon and Na alkyl. An improved prep. of 9 : 10-diisooamyl-9 : 10-dihydroanthracene from *iso*- $\text{C}_5\text{H}_{11}\text{Cl}$, Na, and anthracene is described. Bu^iCl , Na, and 2 : 3- $\text{C}_{10}\text{H}_6\text{Me}_2$ yield 2 : 3-dimethyl-1-isobutyl-1 : 4-dihydronaphthalene, b.p. $150^\circ/0.1$ mm., with a little 2 : 3-dimethyl-1 : 4-diisobutyl-1 : 4-dihydronaphthalene, b.p. $180^\circ/0.1$ mm. Fluoranthene with Na and Bu^iCl affords 1 : 4-diisobutyl-1 : 4-dihydrofluoranthene, b.p. 160° /cathode-ray vac.; a similar product from chrysene could not be distilled. II. N. R.

Induced oxidation of naphthalene with ascorbic acid as inductor. W. P. JORISSEN (Natuurwetensch. Tijds., 1937, 19, 15—16).—Solutions of 0.1 g. of C_{10}H_8 and 0.4 g. of ascorbic acid in 40 c.c. of COMe_2 and 10 c.c. of H_2O contained only oxidation products of C_{10}H_8 [$\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$] after keeping for 2 weeks under aerated conditions. S. C.

[Additive compound of] sodium [and] naphthalene. I. Preparation of additive compounds of alkali metals and polycyclic aromatic hydrocarbons. N. D. SCOTT, J. F. WALKER, and V. L. HANSLEY (J. Amer. Chem. Soc., 1936, 58, 2442—2444).— C_{10}H_8 and Na react rapidly in Me_2O at -30° or, more conveniently, in $(\text{CH}_2\text{OMe})_2$ (I) at -10° to 30° in N_2 to give the additive compound (II), $\text{C}_{10}\text{H}_8\text{Na}_2$ or $\text{C}_{10}\text{H}_8\text{Na}_2\cdot\text{C}_{10}\text{H}_8$. (I) and (II) react slowly at room temp.: $\text{C}_{10}\text{H}_8\text{Na}_2 + 2(\text{CH}_2\text{OMe})_2 \rightarrow \text{C}_{10}\text{H}_{10} + 2\text{NaOMe} + 2\text{OMe-CH:CH}_2$. Reaction between C_{10}H_8

and Na in Me_2O is inhibited by Et_2O , and an excess of Et_2O causes decomp. of any (II) present to C_{10}H_8 and Na. (II) could not be isolated; the solvent appears to be necessary for its existence. (II) reacts with H_2O , alcohols, and compounds (e.g., C_2H_2) which form Na derivatives (A), forming dihydronaphthalene and (A). With O_2 , Hg, and CH_2PhCl , solutions of (II) behave as $\text{C}_{10}\text{H}_8 + \text{Na}$. Me_2O and (I) can be used with other alkali metals and they facilitate reaction between Na and COPh_2 or anthracene. Compounds similar to (II) can be prepared from $\text{C}_{10}\text{H}_7\text{Me}$, Ph_2 , acenaphthene, and phenanthrene in Me_2O (not in Et_2O) or (I). H. B.

Rate of decomposition of tetralin peroxide.

I. Thermal decomposition. II. Effect of quinol. III. Effect of antioxidants. T. YAMADA (J. Soc. Chem. Ind. Japan, 1936, 39, 450—452B, 452—455B, 455—457B).—I. Decomp. of tetrahydronaphthalene (I) peroxide (II) [prep. of sample containing 0.25 mol. of peroxide per mol. of (I) described] at 120° , 130° , and 140° is a first-order reaction (cf. B., 1936, 1055) which is interpreted by a chain mechanism.

II. The rate of decomp. of (II) at 130° in presence of quinol is const. and independent of the concn. of quinol. A chain reaction is postulated.

III. $\alpha\text{-C}_{10}\text{H}_7\text{OH}$, phloroglucinol, gallic and protocatechuic acids, and $o\text{-NH}_2\text{C}_6\text{H}_4\text{OH}$ resemble quinol in their effect on the decomp. of (II). J. L. D.

Sterol hydrocarbon, $\text{C}_{18}\text{H}_{16}$, and two isomerides thereof. H. HILLEMANN (Ber., 1936, 69, [B], 2610—2617; cf. A., 1933, 1154).—After adequate purification the "sterol $\text{C}_{18}\text{H}_{16}$ " (I) of Diels (A., 1933, 1047; 1935, 481) is devoid of fluorescence, which also is not shown by synthetic isomeric hydrocarbons; the absorption spectrum does not indicate the nature of the causative impurity. The m.p., $130\text{--}131^\circ$, assigned by the authors to the picrate (*loc. cit.*) is confirmed. Treatment of 3-acetylphenanthrene with $\text{CH}_2\text{BrCO}_2\text{Me}$ and Zn in boiling C_6H_6 and of the product with POCl_3 affords *Me* β -3-phenanthrylcrotonate, b.p. $201\text{--}205^\circ/0.02\text{ mm.}$, m.p. $56\text{--}57^\circ$, hydrolysed to β -3-phenanthrylcrotonic acid, m.p. $194.5\text{--}196.5^\circ$, which is hydrogenated (Pd-BaSO₄) to β -3-phenanthrylbutyric acid, (II), m.p. $105\text{--}107^\circ$. Cyclisation of (II) by successive action of SOCl_2 and AlCl_3 in PhNO_2 gives 3-methyl-6:7-7':8'-naphthahydrind-1-one (III), m.p. 91° , and 3-methyl-5:6-1':2'-naphthahydrind-1-one (IV), m.p. $140\text{--}141^\circ$. Reduction (Clemmensen) of (III) and (IV) gives 1'-methyl-3:4-, b.p. $172\text{--}173^\circ/0.05\text{ mm.}$, m.p. $28\text{--}29^\circ$, and 3'-methyl-2:3-, m.p. $75\text{--}76^\circ$, -cyclopentenophenanthrene, respectively. Oxidation of (III) and (IV) by HNO_3 (d 1.4) affords, respectively, 1:2:3:4- and 1:2:4:5- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$. The identity of the NO-compounds from (I) and synthetic 3'-methylcyclopentenophenanthrene (*loc. cit.*) is confirmed. *Me* β -3-phenanthrolylpropionate has m.p. $67\text{--}70^\circ$. H. W.

Reduction of aromatic nitro-compounds with sodium stannite. G. LOCK and E. BAYER (Ber., 1936, 69, [B], 2666—2669).—The aromatic NO_2 -compound, if necessary in EtOH , is briskly stirred for 2 hr. at 80° with the amount of Na_2SnO_3 solution calc. for reduction to the azo-stage. PhNO_2 gives 71% of azoxybenzene (I) and 21% of NH_2Ph or under

more drastic conditions 52% of NH_2Ph and a very difficultly separable mixture of much (I) and little PhN_2Ph . $o\text{-C}_6\text{H}_4\text{MeNO}_2$ yields 9% of $o\text{-C}_6\text{H}_4\text{MeNH}_2$ (II) and 87% of oo' -azoxytoluene (III), the proportion of (II) at the expense of (III) being increased if the conditions are more drastic. $m\text{-C}_6\text{H}_4\text{MeNO}_2$ is smoothly reduced to mm' -azoxytoluene without appreciable amounts of other reduction products. $p\text{-C}_6\text{H}_4\text{MeNO}_2$ gives about 15% of $p\text{-C}_6\text{H}_4\text{MeNH}_2$ and a difficultly separable mixture of azoxy- and azo-compounds; $o\text{-C}_6\text{H}_4\text{ClNO}_2$ behaves similarly. $m\text{-C}_6\text{H}_4\text{ClNO}_2$ yields $m\text{-C}_6\text{H}_4\text{ClN}_2\text{C}_6\text{H}_4\text{Cl-}m'$ and $m\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ gives the corresponding azo-compound. $p\text{-C}_6\text{H}_4\text{ClNO}_2$ affords 17% of $p\text{-C}_6\text{H}_4\text{ClNH}_2$ and pp' -dichloroazoxybenzene. Contrary to Witt, therefore, reduction of NO_2 -compounds by Na_2SnO_3 is not a general method for the prep. of azo-derivatives. H. W.

Decomposition of salts of thiocarbamic acid. Mechanism of formation of diarylthiocarbamides. N. S. DROZDOV (J. Gen. Chem. Russ., 1936, 6, 1368—1374).— $(\text{NHPhCS}_2)_2\text{Cu}$ in H_2O at 100° yields PhCNS (I), $\text{CS}(\text{NHPh})_2$ (II), and CuS . In presence of excess of Cu^{++} $\text{CO}(\text{NHPh})_2$ is also obtained, whilst in presence of $(\text{NH}_4)_2\text{CO}_3$ the products are (II) and NH_2CSNHPh (III), and when both excess of Cu^{++} and $(\text{NH}_4)_2\text{CO}_3$ are present (I) and (III) are formed. $(\text{NHPhCS}_2)_2\text{Pb}$ and $(\text{NH}_4)_2\text{CO}_3$ in H_2O at 100° yield (II) and (III). NH_2PhCS_2 and aq. NaOH yield exclusively (II) at 75° , (I) and (II) at $20\text{--}35^\circ$, and (II) and NHPhCS_2Na (IV) at $5\text{--}10^\circ$. The mechanism of the reactions is: $2\text{NH}_2\text{Ph} + 2\text{CS}_2 + 2\text{NaOH} \rightarrow 2(\text{IV}) + 2\text{H}_2\text{O}$; $(\text{IV}) \rightarrow (\text{I}) + \text{NaSH}$; $(\text{IV}) + \text{NaSH} \rightarrow \text{Na}_2\text{CS}_3 + \text{NH}_2\text{Ph}$; $\text{NH}_2\text{Ph} + (\text{I}) \rightarrow (\text{II})$; $\text{NH}_2\text{Ph} + \text{CS}_2 \rightarrow \text{NHPhCS}_2\text{H}$, $\text{NH}_2\text{Ph} \rightarrow (\text{I}) + \text{NH}_2\text{Ph} + \text{H}_2\text{S} \rightarrow (\text{II}) + \text{H}_2\text{S}$; $\text{NHPhCS}_2\text{NH}_4 \rightarrow (\text{III}) + \text{H}_2\text{S}$. R. T.

Action of phenylcarbimide on α -glycols and α -oxides. K. A. KRASUSKI and M. MOVSUM-ZADE (J. Gen. Chem. Russ., 1936, 6, 1203—1207).— PhNCO (I) and $(\text{CH}_2\text{OH})_2$ (15 hr. at 100°) yield exclusively the diphenylurethane. (I) and $\text{OHCH}_2\text{CMe}_2\text{OH}$ in Et_2O (100° ; 40 hr.) afford $\text{CO}(\text{NHPh})_2$ and isobutylene glycol diphenylcarbamate, m.p. 140.5° , whilst pinacol yields analogously the diphenylcarbamate, m.p. 215° . $(\text{CH}_2)_2\text{O}$ and (I) (100° ; 18 hr.) yield Ph_2 isocyanurate, whilst trimethylethylene oxide does not react after 30 hr. at 100° . R. T.

Action of iodine trichloride on acetanilide. E. CLEPAZ (Atti R. Ist. Veneto Sci., 1934—1935, 94, 555—562; Chem. Zentr., 1936, i, 1411—1412).— KClICl_2 in cold CHCl_3 reacts with NHPhAc to yield *N*-dichloriodoacetanilide, NPhAcICl_2 , m.p. 127° (decomp.), which yields $p\text{-C}_6\text{H}_4\text{ClNHAc}$, m.p. 174° , with H_2O , dil. alkali, or when heated. HNO_3 affords 4-chloro-2-nitro-, m.p. 101° , and 4-nitroacetanilide, m.p. 214° . H. N. R.

Rearrangement of *N*-chloroacetanilide in presence of radioactive hydrochloric acid.—See A., I, 87.

Electrochemical reduction of *N*-nitrosomethylaniline.—See A., I, 91.

Action of sodium nitrite on *p*-nitrodimethylaniline in hydrobromic acid. G. J. G. MILTON and T. H. READE (J.C.S., 1936, 1749—1750).— $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ and NaNO_2 (4 mols.) in $>4N\text{-HBr}$ at 0° give 2-bromo-4-nitrodimethylaniline hydrobromide perbromide, m.p. 157° , converted by hot aq. EtOH into 2-bromo-4-nitrodimethylaniline, m.p. 74° . This with NaNO_2 (3 mols.) in HCl at 0° gives 2-bromo-4-nitrophenylmethylnitrosoamine, m.p. 95° , hydrolysed by hot conc. HCl to 2-bromo-4-nitromethylaniline, m.p. 115° , which with warm conc. HNO_3 gives 2-bromo-4:6-dinitrophenylmethylnitrosoamine, m.p. 126° , converted by hot PhOH into 4:6:2-(NO_2) $_2\text{C}_6\text{H}_2\text{Br}\cdot\text{NHMe}$. The limiting [Br] for brominating action of $\text{HNO}_2\text{-HBr}$ mixtures is 0.003 g.-mol. per litre as judged by formation of $\text{NPhMe}_3\text{Br}_3$; it is decreased by addition of NaBr . $\text{NPhMe}_3\text{Br}_3$ in H_2O slowly gives the *m*-Br-compound, Br, and BrO_3^- . R. S. C.

2:4:6-Trichloro-*m*-toluidine and some derivatives. E. BUREŠ and M. TRPIŠOVSKÁ (Časopis českoslov. Lék., 1935, 15, 179—186; Chem. Zentr., 1936, i, 1209).—Chlorination of acet-*m*-toluidide in AcOH affords 2:4:6-trichloroacet-*m*-toluidide, m.p. 192° , hydrolysed (NaOH) to 2:4:6-trichloro-*m*-toluidine, m.p. 85° (Bz, m.p. 218° , and Ac derivative, m.p. $81\text{--}82^\circ$). 2:4:6-Trichloro-, m.p. 38° , and 2:3:4:6-tetrachloro-, m.p. $91.5\text{--}92^\circ$, -toluene are prepared from the appropriate amines by the diazo-reaction; on nitration they yield 2:4:6-trichloro-3-nitrotoluene, m.p. 50° , and 2:3:4:6-tetrachloro-5-nitrotoluene, m.p. $148\text{--}150^\circ$, respectively. 2:4:6-Trichloro-3-bromo-, m.p. 85° , and -2-iodo-, m.p. 63° , -toluene are obtained from the appropriate diazonium salts, Cu-bronze, and KBr or KI. H. N. R.

Nuclear alkylation of aromatic bases. III. Action of methyl alcohol on the hydrochlorides of α - and β -naphthylamine. D. H. HEX and E. R. B. JACKSON (J.C.S., 1936, 1783—1788; cf. A., 1934, 764).—Nuclear alkylation occurs more readily with β - than with $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, but the products are mainly phenolic, owing to ready fission of the C-N linking. $\alpha\text{-C}_{10}\text{H}_6\cdot\text{NH}_2\cdot\text{HCl}$ with 3 mols. of MeOH at $240\text{--}250^\circ$ gives mainly $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$ and tar, but at 220° also some $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NMe}_2$; with 4 mols. at $230\text{--}250^\circ$ much $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$, some 2:1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{OH}$, $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NHMe}$, and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OMe}$, and less tar are formed. $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2\cdot\text{HCl}$ with 3 mols. of MeOH at $200\text{--}220^\circ$ gives $\beta\text{-C}_{10}\text{H}_7\cdot\text{NMe}_2$, $\text{NH}(\text{C}_{10}\text{H}_7)_2$, $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, $\beta\text{-C}_{10}\text{H}_7\cdot\text{OMe}$, 3:4:6:7- and less 2:3:6:7-dibenzacridine; with 4 mols. at $240\text{--}250^\circ$ mainly 1:2- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{OH}$ and NH_2Me are obtained with less of the other products (no $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$). In an attempt to circumvent the very ready hydrolysis of the α -base, $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NMe}_2\cdot\text{HCl}$ (I) and MeOH were heated at $230\text{--}250^\circ$, but the main reaction was $(\text{I}) \rightarrow \text{C}_{10}\text{H}_6\text{Me}\cdot\text{NHMe} + \text{MeCl} \rightarrow \text{C}_{10}\text{H}_6\text{Me}\cdot\text{OH} + \text{NH}_2\text{Me}$. This is in line with the formation of NH_2Me and not NHMe_2 in the above experiments. It is highly probable that hydrolysis precedes methylation. The benzacridines are formed by condensation of $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ and 1:2- $\text{C}_{10}\text{H}_6\text{MeR}$ ($\text{R} = \text{NH}_2$ or OH), the 1-position of the former taking part in preference to the 3-position. R. S. C.

Nitration of phthalonaphthylimides and the facile preparation of 8-nitro- α -naphthylamine. H. H. HODGSON and J. H. CROOK (J.C.S., 1936, 1844—1848).—Nitration of $\alpha\text{-C}_{10}\text{H}_7\cdot\text{N}(\text{CO})_2\text{C}_6\text{H}_4\cdot\text{o}$ occurs exclusively in the C_{10}H_7 nucleus, 60% in the 8-, 28% in the 5-, and 5% in the 4-position. These proportions are but little affected by substitution of the acyl group. 8:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ is probably co-ordinated thus: $\text{O}_2\text{N}\leftarrow\text{NH}_2$. Phthalonaphthylimide gives mainly 8:2- and 5:2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ [picrate, m.p. 208° (decomp.)]. The simpler diacyl derivatives are hydrolysed during nitration. The following are prepared: phthalonaphthylimide, m.p. 185° (lit. $180\text{--}181^\circ$); 3-, m.p. 225° , and 4-nitro-, m.p. 212° , 3-chloro-, m.p. 191.5° , 3:4-, m.p. 170° , and 3:6-dichloro-, m.p. 217° , and tetrachloro-phthalonaphthylimide, m.p. 244° ; succin- α -, m.p. 153° , and - β -naphthylimide, m.p. 218° ; NN-dibenz-, m.p. 198° , and di-*m*-nitrobenzenesulphon- α -naphthalide, m.p. 252° ; malein- α -naphthylamic acid, m.p. 150° ; 8-nitro- α -naphthylamine picrate, m.p. 181° ; *m*-nitrobenzenesulphon-, m.p. 200° (Na salt, $+x\text{H}_2\text{O}$, m.p. $190\text{--}200^\circ$, and anhyd., m.p. 265°), and di-*m*-nitrobenzenesulphon-8-nitro- α -naphthalide, m.p. $198\text{--}199^\circ$; malein-8-nitro- α -naphthylamic acid, m.p. 198° (decomp.). R. S. C.

Acylation of aromatic aminosulphonic acids. N. N. VOROSCHCOV and A. I. TIROV (J. Gen. Chem. Russ., 1936, 6, 1298—1305).—The velocity of acylation of aminosulphonic acids by boiling AcOH or HCO_2H is small, owing to the low concn. of substrates in solution. Addition of NaOAc increases the solubility of 1:6- or 1:7- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ (I), and raises the b.p. of the mixture, thus giving a max. yield of 75% of acetylated product in presence of 2.5 mols. of NaOAc per mol. of (I). Further addition of NaOAc to 4.5 mols. lowers the yield, as a result of salting-out of the Na salt of (I), but as more NaOAc is added the yields again rise, owing to the higher b.p., and to removal of the Na salt of the Ac derivative from the sphere of reaction by the salting-out action of the excess of Na ions. The efficacy of different cations in the reaction varies with the solubility of the salts formed, in the order $\text{K} > \text{Na} > \text{Mg} > \text{Zn}$, both for acetylation and formylation. R. T.

Elimination of halogen during the nitration of halogenonaphthylamines. H. H. HODGSON and R. L. ELLIOTT (J.C.S., 1936, 1762—1764).—Electronic considerations applied to a static Erlenmeyer formula explain differences in basicity and mode of nitration of halogenonaphthylenediamines. 3-Chloro-2-nitro-1-acetnaphthalide and SnCl_2 in HCl-EtOH give 3-chloro-1-N-acetyl-1:2-naphthylenediamine, m.p. 161° (stannichloride); this with Ac_2O in 20% AcOH gives the $\text{NN}'\text{-Ac}_2$ compound, m.p. 317.5° , from which Cl is eliminated by cold HNO_3 (d 1.42) with formation of 3-nitro- NN' -diacetylnaphthylenediamine, m.p. 303° . 3-Chloro-1:2-naphthylenediamine, m.p. 136° (dihydrochloride), is obtained from 2:3:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_5\text{Cl}\cdot\text{NH}_2$ and SnCl_2 . 4-Chloro-, -bromo-, or -iodo-1:2-naphthylenediamine with conc. $\text{HNO}_3\text{-AcOH}$ at 90° gives 4-nitro-2-N-acetyl-1:2-naphthylenediamine, m.p. 245° , also obtained from the 4-halogeno-2-N-acetylnaphthylenediamines and warm aq. HNO_3 . The 2-

halogeno-1-*N*-acetyl-1:4-diamines similarly lose the halogen when nitrated, giving 2-nitro-1-*N*-acetyl-1:4-naphthylenediamine, m.p. 164° [corresponding Ac_2 compound, m.p. 310.5° (cf. lit.)]. 4:1- $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ and SnCl_2 give 1:4- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ [Ac_2 derivative, m.p. 319° (lit. 303–304°)]. 4:1- $\text{NO}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NHAc}$ gives *N*-acetyl-1:4-naphthylenediamine, unstable (*stannichloride*). R. S. C.

New type of condensation of organic compounds by means of alkali metals. Amide condensation. G. V. TSCHELINCEV and E. D. OSETRVA (J. Gen. Chem. Russ., 1936, 6, 1267–1277).—Na and NPh_2Ac in C_6H_6 (3 hr. at the b.p.) yield *acetoacetdiphenylamide* (I), m.p. 86–87°: $\text{NPh}_2\text{Ac} + \text{CH}_2\text{Na} \cdot \text{CO} \cdot \text{NPh}_2 \rightarrow \text{NPh}_2 \cdot \text{CMe}(\text{ONa}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NPh}_2 \rightleftharpoons \text{(I)} + \text{NaNPh}_2 \rightleftharpoons \text{ONa} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO} \cdot \text{NPh}_2 + \text{NHPh}_2$. Na, NPh_2Ac , and COPhMe in Et_2O or C_6H_6 yield $\text{COMe} \cdot \text{CH} \cdot \text{Bz}$. R. T.

cis-trans-Isomeric stilbenes. III. Stereochemistry of R. Pschorr's phenanthrene synthesis. P. RUGGLI and A. STAUB (Helv. Chim. Acta, 1936, 19, 1288–1291).—The Pschorr synthesis of phenanthrene (I) depends on the *cis* relation of the two Ph groups. *o*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{Ph})_2$ and H_2 -Ni in aq. EtOH gives *cis*-2-aminostilbene, an oil, which yields (Pschorr) 34% of (I). Ordinary *o*-aminostilbene compounds are *trans* and give no derivatives of (I). $\text{C}_6\text{H}_4\text{R} \cdot \text{CH} \cdot \text{CPh} \cdot \text{CO}_2\text{H}$ (R = NO_2 or NH_2) are *cis*(Ph)-compounds by repulsion of the Ph and CO_2H , which accounts for the success of the ordinary Pschorr synthesis. R. S. C.

Flavin synthesis. Crystalline intermediate products. P. KARRER and H. MEERWEIN (Helv. Chim. Acta, 1936, 19, 1190–1191).—Hydrogenation (Ni; 70–90°; 20 atm.) of crude 2-*l*-arabityl- or 2-*d*-ribityl-amino-4:5-dimethylazobenzene gives 50–55% yields of *N*-1-arabityl-, m.p. 138° (uncorr.), and *N*-*d*-ribityl-4:5-dimethylphenylenediamine, m.p. 128° (uncorr.), $[\alpha]_D -17.7^\circ$. R. S. C.

Special transformation of some phenylhydroxylamine derivatives. E. JOLLES (Gazzetta, 1936, 66, 717–723).—A further study of the interconversion of substituted succin- and malcin-imides (cf. A., 1936, 459). Maleic anhydride and $\text{NHPh} \cdot \text{NH}_2$ in boiling AcOH yield maleinphenylhydrazide, new m.p. 265°, or, on prolonged boiling in aq. AcOH, phenylhydrazino-succinphenylhydrazide, m.p. 246°. Malein-*p*-chlorophenyl-, m.p. 288°, and - β -naphthyl-hydrazide, m.p. 269–270°, are prepared. Maleinanil and $\text{NHPh} \cdot \text{OH}$ in boiling $\text{C}_5\text{H}_5\text{N}$ form phenylhydroxylaminosuccinanil, m.p. 189°; on prolonged heating of reactants or of product in $\text{C}_5\text{H}_5\text{N}$, anilinomaleinanil, m.p. 238°, is obtained. Similarly phenylhydroxylaminosuccin-*p*-tolylimide, m.p. 190°, gives rise to anilinomalein-*p*-tolylimide, m.p. 215–217°. Citraconanil forms α -phenylhydroxylamino- α' -methylsuccinanil, m.p. 175°, which does not lose H_2O , even in presence of ZnCl_2 . α -Phenylhydrazino- α' -methylsuccin- α -naphthylimide, m.p. 175°, behaves similarly. Citraconphenylhydrazide with $\text{NHPh} \cdot \text{OH}$ yields α -phenylhydrazino- α' -methylsuccinphenylhydrazide, m.p. 191°. E. W. W.

Preparation of thymol from *m*-cresol. IV. Actions of phosphoric acid, zinc chloride, and

acetic acid-sulphuric acid on *m*-tolyl isopropyl ether. K. ONO and M. INOTO (J. Soc. Chem. Ind. Japan, 1936, 39, 361B).— $\text{m-C}_6\text{H}_4\text{Me} \cdot \text{OPr}^i$ (I) with H_3PO_4 (*d* 1.75) at 120–130° affords *m*-cresol and 4- and 6-isopropyl-*m*-tolyl Pr^i ether, but is largely unchanged. (I) with ZnCl_2 at 200° is almost unchanged, as it is with Niederl's reagent (cf. A., 1931, 838; 1932, 510) at 100° or when boiled. J. L. D.

Synthesis of dulcin by the Curtius reaction. P. P. T. SAH and K. S. CHANG (Ber., 1936, 69, [B], 2762–2764).— $\text{p-OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in boiling H_2O yield *p*-ethoxybenzhydrazide, m.p. 126–127° (benzaldehyde-, m.p. 198–199°, and acetophenone-, m.p. 153–154°, -*p*-ethoxybenzoylhydrazide), converted by NaNO_2 and HCl into *p*-ethoxybenzazide which passes when boiled in C_6H_6 and then treated with $\text{EtOH} \cdot \text{NH}_3$ into *p*-ethoxyphenylcarbamide (dulcin), m.p. 160–161°. Similarly $\text{p-OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ is transformed successively into *p*-methoxybenzhydrazide, m.p. 135–136°, *p*-methoxybenzazide, and *p*-anisylcarbamide, m.p. 164–165°. H. W.

Kinetics of reaction between allyl bromide and sodium phenoxide in dissociating solvents.—See A., I, 87.

Exchange reactions of heavy water with organic compounds. I. Phenol, acetanilide, and the formate ion.—See A., I, 87.

Oxidation of safrole and isosafrole by selenium dioxide. P. WIERZCHOWSKI (Rocz. Chem., 1936, 16, 451–458).—Safrole is heated with SeO_2 in EtOH (3 hr. at the b.p.), the product is filtered from pptd. Se, EtOH is removed at 100°, and the residue is extracted with Et_2O . The following substances were identified in the extract: piperonylacetaldehyde (I), α - and β -ketodihydrosafrole, and 1'-ethoxysafrole. isosafrole (II) and SeO_2 yield (I) and α -piperonylpropane α -oxide, m.p. 39–40°. (II) and SeO_2 in xylene (1 hr. at the b.p.) afford a selenide, $\text{C}_{10}\text{H}_8\text{O}_2\text{Se}$, m.p. 122°. R. T.

isoEugenol and its polymerides. I. E. PUXEDDU and (SIGNA.) A. RATTU (Gazzetta, 1936, 66, 700–710).—isoEugenol Me, Et, and Pr^a ethers are polymerised by FeCl_3 (cf. A., 1913, i, 460) to the corresponding diisoeugenol diethers (cf. A., 1912, i, 185), all of which form Br-derivatives (cf. A., 1912, i, 255). Bromodiisoeugenol Pr^a_2 ether has m.p. 70°. Diisoeugenol Me₂ ether (I) is oxidised by CrO_3 to a substance, m.p. 154°, and to tetramethoxyanthraquinone (cf. A., 1931, 954); this is, however, not considered to indicate an anthracene structure in (I). isoEugenol Pr^a ether with HNO_2 yields dioximinodihydroisoeugenol Pr^a ether peroxide, m.p. 76°, converted by KOH into an oxazolone oxime (?), $\text{C}_{13}\text{H}_{16}\text{O}_4\text{N}_2$, m.p. 142°, and reduced (Sn-HCl) to a 1:2:5-oxadiazole, $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2$, m.p. 72°. E. W. W.

Anthracene and cyclobutane structures for polymerides of diisoeugenol. E. PUXEDDU (Gazzetta, 1936, 66, 710–717).—Theoretical; the cyclobutane is preferred to the anthracene structure (cf. A., 1931, 954). E. W. W.

Wandering of halogen atoms in carbon chains and rings. II. Halogen wandering in the

additive products of α -halogeno-ethers and olefines. C. D. NENITZESCU and V. PRZEMETZKI (Ber., 1936, 69, [B], 2706—2707).—*cyclo*Hexene and $\text{CH}_2\text{Cl}\cdot\text{OMe}$ in CS_2 containing ZnCl_2 at 0° yield 2-chloro-1-methoxymethylcyclohexane, b.p. $88\text{--}91^\circ/17\text{ mm.}$, converted by AlCl_3 in C_6H_6 at $60\text{--}65^\circ$ into 4-phenyl-1-methoxymethylcyclohexane, b.p. $118\text{--}120^\circ/2\text{ mm.}$, which is dehydrogenated by Pt at about 310° and then oxidised to $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$. Wandering is therefore not a sp. effect of CO or CO_2H , but due to a general repelling action of O of any function.

H. W.

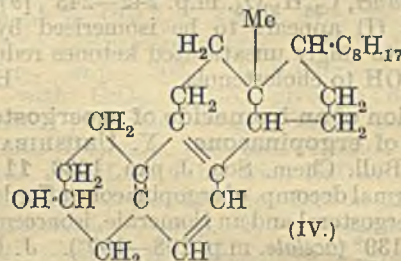
Mesitylene derivatives. Formation of an ether from chloride [ω -chloro-derivatives] and methyl alcohol. W. T. NAUTA and J. W. DIENSKKE (Rec. trav. chim., 1936, 55, 1000—1006).—Me or CH_2Cl in the 2, 4, and 6 positions of CH_2PhCl increases the conductivity in liquid SO_2 and causes unusual reactivity. Mesitylene, aq. CH_2O (1 mol.), and HCl gas at 65° give 2:4:6-trimethylbenzyl chloride (I) m.p. 37° , b.p. $114\text{--}115^\circ/10\text{ mm.}$, μ in SO_2 at -10° 0.013 (CH_2PhCl 0.0013; CPh_3Cl 7.7), and 2:4-di(chloromethyl)mesitylene (II), m.p. 105° ; 2 mols. of CH_2O lead to much (II) and a little (I). (I) immediately ppts. AgCl from $\text{AgNO}_3\text{--EtOH}$; with AgOAc in AcOH at 100° it affords 2:4:6-trimethylbenzyl acetate (III), b.p. $136\text{--}137^\circ/15\text{ mm.}$, hydrolysed by hot 15% aq. KOH to the alcohol, m.p. $88\text{--}89^\circ$; with hot $N\text{-KOH--MeOH}$ or --EtOH it gives 2:4:6-trimethylbenzyl Me (IV), b.p. $109\text{--}110^\circ/15\text{ mm.}$, and Et ether, b.p. $114\text{--}115^\circ/14\text{ mm.}$, respectively. (III) and 2% HCl-MeOH give much (IV) and some (I). (IV) and $N\text{-HCl--MeOH}$ slowly give (I). (I) itself slowly reacts with hot MeOH. $\text{CH}_2\text{Ph}\cdot\text{OAc}$ and HCl-MeOH give some CH_2PhCl , but no $\text{CH}_2\text{Ph}\cdot\text{OMe}$. (II) and AgOAc afford similarly 2:4-diacetoxymethyl-, m.p. $91\text{--}92^\circ$, and -di(hydroxymethyl)-mesitylene, m.p. $188\text{--}189^\circ$. (II) and $N\text{-KOH--MeOH}$ or --EtOH give 2:4-dimethoxy-, m.p. $67.5\text{--}68.5^\circ$, and -diethoxymesitylene, m.p. $57\text{--}58^\circ$, respectively. R. S. C.

cis-cyclo-Hexanediol from cyclohexene oxide. R. CRIEGEE and H. STANGER (Ber., 1936, 69, [B], 2753—2757).—The mono- p -toluenesulphonate of trans-cyclohexane-1:2-diol (I), m.p. $96\text{--}96.4^\circ$, is obtained in 90% yield from cyclohexene oxide (II) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ in anhyd. Et_2O . It is also obtained (37% yield) accompanied by the corresponding acetate by addition of 30% H_2O_2 to cyclohexene (III) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ in AcOH, in 48% yield accompanied by trans-cyclohexanediol (III) by gradual addition of $\text{H}_2\text{O}_2\text{--Et}_2\text{O}$ to (III) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ and from (IV) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$. (III) and 2:5- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{SO}_3\text{H}$ in AcOH containing Ac_2O afford trans-cyclohexane-1:2-diol 2':5'-dichlorobenzenesulphonate, m.p. 134° (corr.; decomp.) [acetate, m.p. 170° (corr.; decomp.)]. (II) and an excess of $\text{CCl}_2\cdot\text{CO}_2\text{H}$ in anhyd. Et_2O give trans-cyclohexane-1:2-diol monotrichloroacetate, m.p. $76\text{--}77^\circ$ (corr.). trans-cyclohexane-1:2-diol di- p -toluenesulphonate, m.p. 109° (corr.), from (I) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$, is remarkably stable to acid and alkali. cis-cyclohexane-1:2-diol di- p -toluenesulphonate, m.p. $128.5\text{--}129.5^\circ$, could not be partly hydrolysed. Treatment of (I) with KOAc in boiling MeOH yields $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{K}$,

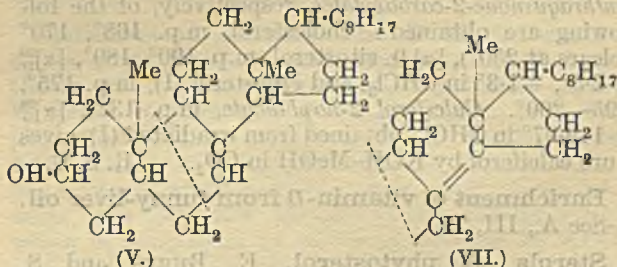
(II), and a fraction of b.p. $118\text{--}120^\circ/12\text{ mm.}$, which gives (IV) when hydrolysed; the first stage in the change appears to be the formation of (II), since a similar product is derived from (II), KOAc, AcOH, and EtOH. trans-cyclohexane-1:2-diol acetate p -toluenesulphonate, m.p. $78\text{--}79^\circ$, from (I) and Ac_2O containing a little conc. H_2SO_4 , is transformed by KOAc in boiling EtOH with subsequent hydrolysis into cis-cyclohexane-1:2-diol, m.p. $96\text{--}98^\circ$ (yield 68%). Better yields (89%) are obtained in boiling AcOH. With AcOH alone the change is unimol.

H. W.

7-Dehydrocholesterol. F. SCHENCK, K. BUCHHOLZ, and O. WIESE (Ber., 1936, 69, [B], 2696—2705).—The differences in the recorded m.p. of 7-dehydrocholesterol (I) are attributed to the presence of solvent of crystallisation. After separation from MeOH and desiccation at room temp. (I) has m.p. $143\text{--}144^\circ$, whereas if dried at $100^\circ/\text{vac.}$ or crystallised from EtOAc it has m.p. 149° after softening at 148° . 7-Dehydrocholesteryl acetate (II) unites slowly with maleic anhydride in boiling xylene to the adduct, $\text{C}_{33}\text{H}_{48}\text{O}_5$, m.p. 178° . Exposure to sunlight of (I) in EtOH containing eosin leads to "7-dehydrocholesterolpinacol" (III), $\text{C}_{27}\text{H}_{44}\text{O}_3\cdot 1.5\text{H}_2\text{O}$, m.p. $196\text{--}197^\circ$ (decomp.), converted by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ into the corresponding diacetate, m.p. $201\text{--}202^\circ$ (decomp.), $[\alpha]_D^{25} -161.2^\circ$ in CHCl_3 , also obtained by insolation of (II). (III) is decomposed when heated above its

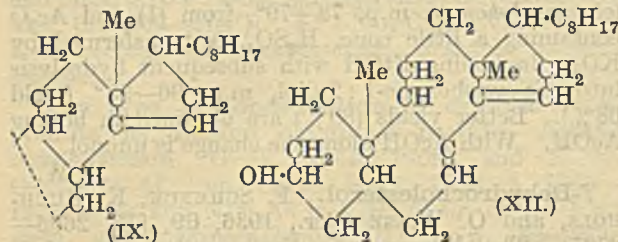


m.p. or boiled with Ac_2O and then hydrolysed into norsterol (IV), m.p. 111° , $[\alpha]_D^{25} +106^\circ$ in CHCl_3 [3:5-dinitrobenzoate, m.p. 207° (decomp.), $[\alpha]_D^{25} -2.5^\circ$ in CHCl_3]. Insolation of (I) in presence of eosin and O_2 gives 7-dehydrocholesterol peroxide, $\text{C}_{27}\text{H}_{44}\text{O}_3$, m.p. 152° , $[\alpha]_D^{25} +6.55^\circ$ in CHCl_3 , reduced by Zn dust in KOH--



EtOH to a cholestenetriol, $\text{C}_{27}\text{H}_{46}\text{O}_3$, m.p. 211° (decomp.). (I) is reduced by Na and abs. EtOH to γ -cholestenol (V), m.p. $122\text{--}123^\circ$, $[\alpha]_D -13.5^\circ$ [acetate (VI), m.p. $118\text{--}119^\circ$, $[\alpha]_D \pm 0^\circ$; benzoate, m.p. $157\text{--}158^\circ$ becoming clear at 176° , $[\alpha]_D^{18} +7.14^\circ$ in CHCl_3]. (V) is transformed by BzO_2H in CHCl_3 into cholestane-3:7:8-triol, m.p. 192° , converted by Ac_2O and $\text{C}_5\text{H}_5\text{N}$ into the diacetate, m.p. $164\text{--}165^\circ$.

Contact of (VI) with Pt in cold EtOAc-Et₂O causes isomerisation to α -cholesteryl acetate, m.p. 77–78°, $[\alpha]_D^{25} +9.46^\circ$ in CHCl₃, also obtained by hydrogenation (Pd sponge in EtOAc) of (II); it is hydrolysed to α -cholesterol (VII), m.p. 119–120°, $[\alpha]_D^{25} +20.36^\circ$



in CHCl₃ [benzoate (VIII), m.p. about 140° after becoming cloudy at about 115°, $[\alpha]_D^{25} +8.53^\circ$ in CHCl₃]. (VIII) is isomerised by HCl in CHCl₃ to β -cholesteryl benzoate, m.p. 168°, $[\alpha]_D^{25} +32.54^\circ$ in CHCl₃, whence β -cholesterol (IX), m.p. 130–131°, $[\alpha]_D^{25} +34^\circ$ in CHCl₃ [acetate (X), m.p. 91–92°]. Hydrogenation (Pt sponge in EtOAc-Et₂O) of (X) yields cholestanyl acetate. 7-Dehydrocholesteryl benzoate is transformed by HCl in CHCl₃ at 0° into dehydrocholesteryl-B₂ benzoate (XI), m.p. 149–150°, $[\alpha]_D^{25} -115.1^\circ$ in CHCl₃, hydrolysed by KOH in MeOH-Et₂O to dehydrocholesterol-B₂ (XII), m.p. 117–118°, $[\alpha]_D^{25} -145.5^\circ$ in CHCl₃ [acetate, m.p. 86–87°, $[\alpha]_D^{25} -114.5^\circ$ in CHCl₃]. (XI) and maleic anhydride in boiling C₆H₆ give the adduct, C₃₈H₅₀O₅, m.p. 242–243°, $[\alpha]_D^{25} -17^\circ$ in CHCl₃. (I) appears to be isomerised by finely divided Ni to singly unsaturated ketones reduced by Na and EtOH to cholestenols. H. W.

Formation of an isomeride of neoergosterol by pyrolysis of ergopinacone. Y. URUSHIBARA and T. ANDO (Bull. Chem. Soc. Japan, 1936, 11, 757–758).—Thermal decomp. of ergopinacone affords a mixture of neoergosterol and an isomeride, isoneoergosterol, m.p. 138–139° (acetate, m.p. 108–109°). J. D. R.

2-Naphthoates and anthraquinone-2-carboxylates of vitamin-D and other sterols. M. SUMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 252–257).—By treatment of a hot C₅H₅N solution with 2-C₁₀H₇-COCl in C₆H₆ or anthraquinone-2-carboxyl chloride alone or in C₆H₆ 2-naphthoates and anthraquinone-2-carboxylates, respectively, of the following are obtained: cholesterol, m.p. 168°, 170° (clears at 250°), $[\alpha]_D^{25}$ 0, sitosterol, m.p. 190°, 189°, $[\alpha]_D^{25} +2.5^\circ$, -1.3° in CHCl₃, and ergosterol (I), m.p. 175°, 195–200°. Calciferol 2-naphthoate, m.p. 132°, $[\alpha]_D^{25} +149.97^\circ$ in CHCl₃, obtained from irradiated (I), gives pure calciferol by KOH-MeOH in CO₂. R. S. C.

Enrichment of vitamin-D from tunny-liver oil.—See A., III, 79.

Sterols. A phytosterol. E. BUREŠ and S. LISIEVÁ (Rep. III Congr. Slav. Pharm., 1934, 213–220).—Repeated hydrolysis of the oil of the seeds of the black henbane (*Hyoscyamus niger*, L.) and extraction with Et₂O gave a phytosterol (I), C₂₈H₄₈O, H₂O, m.p. 119–120°, characterised by the Salkowski reaction and $[\alpha]_D^{25} -29.4^\circ$ in CHCl₃ [acetate (II), m.p. 124°, $[\alpha]_D^{25} -26.5^\circ$ in CHCl₃; benzoate, m.p. 123–124°], converted by PCl₅ into a mixture of Cl₁-

and Cl₂-compounds. The I val. of (I) was 118.6 corresponding with two ethylenic linkings, whilst (II) with Br gave a Br-derivative. Reduction of (I) with H₂ (Ladenburg) gave the H₆-compound, I val. 52.68, no longer giving the Salkowski reaction and slowly absorbing Br. F. R.

Raphanosterol and some of its derivatives. E. BUREŠ and E. SEDLÁŘ (Rep. III Congr. Slav. Pharm., 1934, 221–227).—Repeated hydrolysis and extraction of the oil of the seeds of the wild radish (*Raphanus raphanistrum*, L.) gave a phytosterol, raphanosterol (I), C₂₇H₅₄·OH, m.p. 136°, $[\alpha]_D^{25} -32.19^\circ$ in CHCl₃ [acetate, m.p. 125°, and benzoate, m.p. 139°, both converted by Cl₂ in CHCl₃ into the corresponding Cl₂-compounds, m.p. 160° and 124°, respectively]. (I) and PCl₅ gave the chloride, m.p. 103°, converted by Cl₂ in CHCl₃ into the Cl₂-compound, m.p. 113°, and reduction of (I) with Na and C₅H₁₁·OH gave a H₂-derivative, m.p. 155°. The OH is therefore alcoholic and (I) contains one ethylenic linking. F. R.

Œstriolglycuronide.—See A., III, 74.

Kinetics of thermal cis-trans isomerisation.

VI. [β -Cyanostyrene].—See A., I, 86.

Tenacity of organic radicals and reactivity. III. Hydrolysis of esters and reduction of nitro-compounds. K. KINDLER [with K. G. ELLINGER, W. FÜRST, and H. SCHMIDT] (Ber., 1936, 69, [B], 2792–2810).—The rate of hydrolysis of esters, R·CO₂Et, and of addition of H₂S to nitriles, R·CN, increases as the firmness of the union of R to ·CO₂Et or ·CN diminishes. Further, compounds R·NO₂ are reduced more rapidly by TiCl₃ as the tenacity of R declines. Experimentally, the first and third methods are the most accurate. A general parallelism is observed in the data given by the three methods, but exact mathematical agreement is neither expected nor attained. The tenacity of alkyl radicals increases markedly from Me to Prⁿ and then slowly. *n*-Alkyls are more loosely attached than those with branched chains. The unsaturated oleic residue is more firmly united than the saturated stearic group. *p*-Substituted aryls with negative substituents cling more loosely, those with positive substituents more strongly, than Ph. *p*-Me, -Et, or -Prⁿ behaves very similarly to *p*-CO₂Et. Both position and nature influence the tenacity of aryls. Increase in the no. of NO₂ groups causes marked decline in tenacity. In general, aralkyl groups are less firmly united than the corresponding alkyl radicals. CHAr·CH· is much more firmly joined than CH₂Ar·CH₂·. 2-, 3-, and 4-Pyridyl, 2-, 3-, and 4-quinolyl, and 2-isoquinolyl are less firmly attached to ·CO₂Et than Ph. Me and OMe in quinolyl behave as when in the *p*-position in aryls. 2-Thienyl closely resembles Ph, but 2-furfuryl is much more loosely combined. The sequence of tenacity towards ·CO₂Et, ·CN, and ·NO₂ is the same as that observed previously towards halogens and now established by the rate of reaction of R·COCl and NaOEt. The following compounds appear new: *Et p-n-propylbenzoate*, b.p. 143°/18 mm. (corresponding acid, m.p. 142.5°); *Et p-n-propoxybenzoate*, b.p. 193–194°/9 mm.; *Et p-isopropoxybenzoate*, b.p. 157–160°/9

mm.; *Et* *p*-isooctoxybenzoate, b.p. 201—203°/9 mm.; *Et* quinoline-2-carboxylate, b.p. 186—188°/13 mm.; *Et* quinoline-3-carboxylate, b.p. 174°/10 mm., m.p. 66—67° [corresponding acid, m.p. 282—283° (decomp.)]; *Et* 4-methylquinoline-2-carboxylate, b.p. 198—200°/13 mm., m.p. 33—36°; *Et* 8-methylquinoline-2-carboxylate, b.p. 181—182°/12 mm. H. W.

Synthesis of diphenyl acetates. N. N. CHATTERJEE (J. Indian Chem. Soc., 1936, 13, 593—598; cf. A., 1935, 1496).—*Et* 4-methylcyclohexanone-2-carboxylate with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ and $\text{NaOEt}\cdot\text{EtOH}$ (or $\text{Na}\cdot\text{C}_6\text{H}_6$) gives *Et*₂ 4-methylcyclohexanone-2-carboxylate-2-acetate (I), b.p. 165°/5 mm. (semicarbazone, m.p. 174°), hydrolysed by $\text{HCl}\cdot\text{H}_2\text{O}$ to 4-methylcyclohexanone-2-acetic acid, b.p. 160—165°/6 mm. [*Et* ester (II), b.p. 129°/8 mm. (semicarbazone, m.p. 210—211°)]. (II) with $\text{MgPhBr}\cdot\text{Et}_2\text{O}$ gives *Et* 1-hydroxy-4-methylhexahydrodiphenyl-2-acetate, b.p. 168—178°/8 mm., reduced by S (200—240°; 4—5 hr.) to *Et* 4-methyldiphenyl-2-acetate, b.p. 160—167°/6 mm., and converted by $\text{SOCl}_2\cdot\text{C}_6\text{H}_5\text{N}\cdot\text{Et}_2\text{O}$ into *Et* hexahydrodiphenyl-2-acetate, b.p. 165—175°/7 mm., hydrolysed to the corresponding acid, m.p. 168—170°. (I) when treated with $\text{MgPhBr}\cdot\text{Et}_2\text{O}$ and then with H_2SO_4 gives the lactone, m.p. 112°, b.p. 200—220°/7 mm., of 1-hydroxy-2-carbethoxy-4-methylhexahydrodiphenyl-2-acetic acid. The following have been prepared by similar methods. *Et*₂ 5-, b.p. 163—166°/5 mm. (cf. lit.), and *Et*₂ 6-, b.p. 158—162°/8 mm., -methylcyclohexanone-2-carboxylate-2-acetate; 5-, m.p. 94—95°, b.p. 162°/4 mm. [*Et* ester, b.p. 127°/5 mm. (semicarbazone, m.p. 174—175°)] (cf. lit.), and 6-methylcyclohexanone-2-acetic acid, b.p. 162—166°/6 mm. (*Et* ester, b.p. 125—130°/8 mm.); *Et* 1-hydroxy-5-, b.p. 165—175°/7 mm., and -6-, b.p. 160—170°/7 mm., -methylhexahydrodiphenyl-2-acetate; *Et* 5-, b.p. 160—165°/6 mm., and *Et* 6-, b.p. 160—163°/9 mm., -methyldiphenyl-2-acetate; lactone, b.p. 210—220°/7 mm., of 1-hydroxy-2-carbethoxy-5-methylhexahydrodiphenyl-2-acetic acid and the lactone, b.p. 205—215° of the corresponding -6-Me-compound.

H. G. M.

Decomposition of methoxymethyl salicylate. Prismatic crystals of salicylic acid. V. A. IZMAILSKI and B. M. BOGOSLOVSKI (J. Gen. Chem. Russ., 1936, 6, 1193—1197).—A sample of methoxymethyl salicylate (I) had undergone decomp. after remaining for 8 years in a stoppered bottle, at room temp., to yield a mixture of products, of which salicylic acid (II), 2-hydroxy-3-aldehydobenzoic acid, 2-hydroxyisophthalic acid, and 3-hydroxymethylsalicylic acid (III) were identified. The probable reactions are: $(\text{I}) + \text{H}_2\text{O} \rightarrow (\text{II}) + \text{CH}_2\text{O} + \text{MeOH}$; $(\text{II}) + \text{CH}_2\text{O} \rightarrow (\text{III})$. The (II) crystallises from the reaction mixture in the form of rectangular prisms.

R. T.

Phenacylthiolacetic acid and related compounds. B. HOLMBERG (Arkiv Kemi, Min., Geol., 1936, 12, A, No. 9, 11 pp.).—Interaction of $\text{COPh}\cdot\text{CH}_2\text{Br}$ (I) with $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (II) in NaOH affords $\text{CH}_2\text{Bz}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III) (Behagel *et al.*, A., 1935, 1237) (oxime, m.p. 125—127°, reduced by $\text{Na}\cdot\text{Hg}$ to a substance, $\text{C}_{18}\text{H}_{22}\text{O}_3\text{N}_2\text{S}$). When steam-distilled with $\text{N}\cdot\text{NaOH}$, (III) gives COPhMe and

$\text{CH}(\text{CH}_2\text{Bz})_2\cdot\text{CO}_2\text{H} + \text{C}_6\text{H}_6$, m.p. 133.5—134.5°, and solvent-free, identical with a specimen prepared by Bougault's method (A., 1909, i, 487). Condensation of (II) with either (III) or $\text{COPh}\cdot\text{CH}_2\cdot\text{OH}$ in presence of 5*N*-HCl at 100° affords $\beta\beta$ -di(carboxymethylthiol)- β -phenylethylthiolacetic acid, $\text{CPh}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (IV), m.p. 147—150°, stable to $\text{N}\cdot\text{NaOH}$ at 100°. (I) and (II) in Et_2O afford (III) and the products of an oxidation-reduction reaction: $(\text{I}) + 2(\text{II}) \rightarrow \text{COPhMe} + \text{HBr} + (\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, but since both products react with (II) the presence of this reagent in excess affords (IV) and an oil, seeming to be mainly $\text{CPh}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2\cdot\text{CH}_2\cdot\text{OH}$. Oxidation of (III) with aq. $\text{K}_2\text{S}_2\text{O}_8$ with cooling gives phenacylthionylacetic acid, two forms, m.p. 85—86°, m.p. 124—125° (decomp.), decomposed by alkali thus: $\text{CH}_2\text{Bz}\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na} + \text{NaOH} \rightarrow \text{COPhMe} + \text{ONa}\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$. J. W. B.

Introduction of double linkings into bile acids and sterols. I. Bromination of 3-ketocholanic acid and of cholestenone. E. DANE, Y. WANG, and W. SCHULTE (Z. physiol. Chem., 1936, 245, 80—88).—3-Ketocholanic acid in AcOH with 2*N*-Br in AcOH gives a 35% yield of 4-bromo-3-ketocholanic acid (I), m.p. 179° (decomp.), which with KOH in MeOH gives 4-hydroxy-3-ketocholanic acid, m.p. 186°. (I) when boiled with $\text{C}_5\text{H}_5\text{N}$ gives 3-keto- Δ^4 -cholanic acid, m.p. 178°, in 49% yield (Me ester, m.p. 126°). Cholestenone in $\text{CHCl}_3 + \text{AcOH}$ with Br in AcOH gives 2:4-dibromocholestenone, $\text{C}_{27}\text{H}_{42}\text{OBr}_2$ or $\text{C}_{24}\text{H}_{40}\text{OBr}_2$, m.p. 203°. 5:6-Dibromocholesterol oxidised with CrO_3 at 45° gives 5:6-dibromocholestanone (II) and with KMnO_4 6-bromo- Δ^4 -cholestenone (III), m.p. 132°, also obtained by boiling (II) in abs. EtOH for 1 hr. with NaOAc . (II) and (III) boiled for several hr. with HCl in MeOH give 3:6-cholestanedione, m.p. 170° [disemicarbazone, m.p. 203° (decomp.)]. (III) with 6% AgNO_3 in $\text{C}_5\text{H}_5\text{N}$ at room temp. gives $\Delta^{4,6}$ -cholestadienone [semicarbazone, m.p. 218° (decomp.)], with boiling $\text{C}_5\text{H}_5\text{N}$ a substance, m.p. 276°, and cholestenone, m.p. 83° (oxime, m.p. 179°), and with KOH in MeOH in 3 hr. at room temp. followed by treatment with semicarbazide acetate the semicarbazone, m.p. 222° (decomp.), of 6-hydroxy- Δ^4 -cholestenone. W. McC.

Syntheses of 2-amino- and 2-chloro-3-methoxy-4-ethoxybenzoic acid and attempted synthesis of 3-methoxy-4-ethoxy-*o*-phthalic acid. K. FEIST, W. AWE, and W. VÖLKSEN (Ber., 1936, 69, [B], 2743—2749).—2-Nitrovanillin is ethylated by $\text{KOH}\cdot\text{Et}_2\text{SO}_4$ or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Et}$ to 2-nitro-3-methoxy-4-ethoxybenzaldehyde (I), m.p. 112° [semicarbazone, m.p. 247—248° (decomp.)], the constitution of which is established by its transformation by KOH and COMe_2 into 7:7'-dimethoxy-6:6'-diethoxyindigotin, m.p. 290°. (I) is oxidised by a large excess of KMnO_4 to 2-nitro-3-methoxy-4-ethoxybenzoic acid, m.p. 190—191° [*Me* ester (II), m.p. 92°], reduced by $\text{NH}_3\cdot\text{FeSO}_4$ to 2-amino-3-methoxy-4-ethoxybenzoic acid (III), m.p. 183° [*Me* ester (IV), m.p. 42°], obtained also by reduction of (II) with Sn and HCl . Diazotisation of (III) in 2*N*-HCl followed by treatment with $\text{K}_3\text{Cu}(\text{CN})_4$ unexpectedly leads to 2-chloro-3-methoxy-4-ethoxy-

benzoic acid, m.p. 177° (non-cryst. *Me* ester). Analogously, 2-aminoveratric acid yields 2-chloroveratric acid, m.p. 169°, or 2-bromoveratric acid if HBr replaces HCl; in complete absence of halogen hemipinic acid is obtained in very small amount. Diazotisation of (III) in 2*N*-H₂SO₄ followed by hydrolysis of the nitrile yields small amounts of material, m.p. 155—157°, apparently a mixture of mono- and di-carboxylic acids; under more drastic conditions decarboxylation occurs with production of 3:4-OMe-C₆H₃(OEt)-CO₂H (V), m.p. 194°. Diazotisation of (IV) in 2*N*-H₂SO₄ and treatment of the product with K₃Cu(CN)₄ gives *Me* 2-cyano-3-methoxy-4-ethoxybenzoate, m.p. 107°, in good yield; it is unaffected by cold HCl-Et₂O but hydrolysed by 10—15% KOH-MeOH to (V). Possibly the dicarboxylic acid is obtained by use of 2% KOH at 100°. H. W.

Derivatives of hydroxyphenylmaleimide. V. HARLAY (J. Pharm. Chim., 1936, [viii], 24, 537—549).— α -Hydroxy- α' -phenylmaleimide (I) gives with 2*N*-NaOH CH₂Ph-CO-NH₂ and with *N*-NaOH, *phenylpyruvimide*, m.p. 156—157°. (I) and Me₂SO₄ in aq. alkaline solution afford the *N-Me* derivative (II), m.p. 207—208°, which with EtI in a bomb tube gives the *Et* ether of (II), m.p. 53. (I) and CH₂O yield the *N-hydroxymethyl* derivative of (I), m.p. 207°. NaOCl, NaOBr, and NaOI in the presence of insufficient alkali give lachrymatory oils; with excess they give CHPhCl-CO-NH₂, CHPhBr-CO-NH₂, and α -iodo-phenylacetamide, m.p. 150°. R. F. P.

Preparation of the ten dicyanonaphthalenes and the related naphthalenedicarboxylic acids. E. F. BRADEROOK and R. P. LINSTED (J.C.S., 1936, 1739—1744).—The following dicyanonaphthalenes are prepared in the yields stated from the pure alkali cyanonaphthalenesulphonates and K₃Fe(CN)₆ or KCN at 320—390° (occasionally only at higher temp.)/40 mm. in CO₂ or (usually) in lower yield from the crude sulphonates: 1:2-, m.p. 190° (75%), 1:3*, m.p. 179° (17%), 1:4-, m.p. 208° (71%), 1:5-, m.p. 263° (53%), 1:6-, m.p. 211° (18%), 1:7*, m.p. 167° (>31%), 1:8*, m.p. 232° (9%), 2:6-, m.p. 293° (42%), and 2:7-, m.p. 267° (8%). Substances marked * are new. Regularities in the variations of yields are discussed; the SO₃H is activated by the CN if separated therefrom by an ethylenic linking or a conjugated system of such linkings. Hydrolysis by boiling aq. H₂SO₄-AcOH gives 1:2-, m.p. 168° (*Me* H, m.p. 145°, and *Me*₂ ester, m.p. 85°), 1:3-, m.p. 267—268°, 1:4-, m.p. >300° [*Me*₂ ester, m.p. 67° (lit. 64°)], 1:5-, m.p. >300° [*Me*₂ ester, m.p. 119° (cf. lit.)], 1:6- (*Me*₂ ester, m.p. 98°), 1:7- (*Me*₂ ester, m.p. 90°), 1:8- (*Me*₂ ester, m.p. 104°), 2:6-, m.p. >300° (*Me*₂ ester, m.p. 186°), and 2:7- (*Me*₂ ester, m.p. 135°)-naphthalenedicarboxylic acid. The following are incidentally described: *Na* 2-cyanonaphthalene-1-, -3-, -5-, and -8-sulphonate, *K* 1-cyanonaphthalene-4-sulphonate, *Na* 2-cyanonaphthalene-6- and -7-sulphonate.

[With A. R. LOWE.] 2:3-NH₂-C₁₀H₆-CO₂H gives (Sandmeyer) 2:3-naphthalimide (cf. lit.), which, when passed in NH₃ over ThO₂ at 490°, gives 2:3-

dicyanonaphthalene, m.p. 251°, and thence the *Me*₂ dicarboxylate, m.p. 47°. R. S. C.

spiro-Compounds. II. Ring transformation into spiro-compound from 4-methylcyclohexanone. New synthesis of cadalene. N. N. CHATTERJEE (J. Indian Chem. Soc., 1936, 13, 588—592; cf. this vol., 19).—4-Methylcyclohexanonecyanohydrin when treated with CN·CHNa·CO₂Et-EtOH (3 days) and then mixed with CH₂Cl·CH₂·CO₂Et and boiled gives *Et*₂ 1-cyano-4-methylcyclohexane-1-cyanoglutarate, b.p. 208—215°/4 mm., hydrolysed by H₂SO₄ and then by NaOH to 1-carboxy-4-methylcyclohexane-1- α -glutaric acid, m.p. 155° [*Et*₂ ester (I), b.p. 175—180°/5 mm.; *Et* ester, m.p. 79°, obtained from the anhydride with EtOH-H₂SO₄]. (I) when heated with Na in C₆H₆ gives *Et*₂ 4-methylcyclohexanespiro-cyclopentan-2'-one-3':5'-dicarboxylate, b.p. 180—185°/4 mm., hydrolysed by dil. H₂SO₄ to 4-methylcyclohexanespiro-cyclopentan-2'-one-5'-carboxylic acid, m.p. 130° [semicarbazone, m.p. 228°; *Et* ester (II), b.p. 133°/4 mm.], oxidised by HNO₃ to hexahydro-*p*-toluic acid. (II) with MgMeI-Et₂O gives the compound

CHMe- $\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix}$ -C- $\begin{matrix} \text{CH}(\text{CMe}_2\cdot\text{OH})\cdot\text{CH}_2 \\ \text{CMe}(\text{OH})\cdot\text{CH}_2 \end{matrix}$, which when heated with Se (290—300° for 20 hr. and then 330° for 30 hr.) gives cadalene (III). This result suggests that the formation of (III) or eudalene on S or Se dehydrogenation of certain sesquiterpenes is not trustworthy evidence for their naphthalene-like ring structure. H. G. M.

Synthetic experiments in the naphthalene and phenanthrene series. B. K. MENON (J.C.S., 1936, 1775—1777).—*p*-C₆H₄Br-CH₂-CO₂Et, NaOEt, and OEt·CH·C(CO₂Et)₂ first at 0° and then at 145—155° give *Et*₂ 7-bromo-1-naphthol-2:4-dicarboxylate, m.p. 105°, hydrolysed to the corresponding acid, m.p. 299° (decomp.) [*Me* ether, m.p. 261° (*dianilide*, m.p. 260°)]. *p*-C₆H₄Cl-CH₂-CO₂Et gives similarly α -*p*-chlorophenylglutaconic acid, m.p. 175° (obtained from the impure *Et*₂ ester, b.p. about 192°/2 mm.), and *Et*₂ 7-chloro-1-naphthol-2:4-dicarboxylate, m.p. 102—103° [corresponding acid, m.p. 294° [*Me* ether, m.p. 228° (*dianilide*, m.p. 215°)]]]. 1-C₁₀H₇-CH₂-CO₂Et yields α -1-naphthylglutaconic acid, m.p. 171°, and 1-phenanthrol-2:4-dicarboxylic acid, m.p. 304° (*Me* ether, m.p. 228°). Decarboxylation of the acids gives only poor yields. R. S. C.

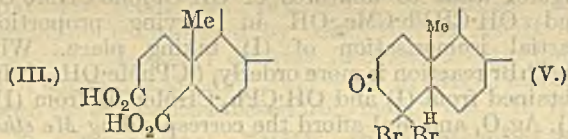
Synthesis of resorcybutyrolactone mono- and di-methyl ethers. K. SUSUKI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 71).— γ -Keto- γ -2-hydroxy-4-methoxy- and -2:4-dimethoxy-phenylbutyric acid with Na-Hg and dil. AcOH give γ -2-hydroxy-4-methoxy-, m.p. about 110—114°, and γ -2:4-dimethoxy-phenylbutyrolactone, m.p. 95—98°, respectively. R. S. C.

Enolic form of acid anhydrides in the Perkin synthesis. P. KALNIN (Ber., 1936, 69, [B], 2843; cf. A., 1929, 63).—A claim for priority in the conception that Perkin's synthesis involves the condensation of the aldehyde with the enolic form of the acid anhydride. H. W.

Action of hydrocyanic acid on active 3-methylcyclohexanone. M. GODCHOT and (MLLE.) G.

CAUQUIL (Compt. rend., 1936, 203, 1042—1044).—The NaHSO_3 compound of 3-methylcyclohexanone ($[\alpha]_{589}^{20} +13.6^\circ$) with HCN at 100° yields 1-cyano-3-methylcyclohexyl 3'-methylcyclohexyl ether, m.p. 146° , $[\alpha]_{5461}^{20} -30.63^\circ$ in C_6H_6 , a compound, $\text{C}_{15}\text{H}_{26}\text{O}_3$, m.p. 96° , $[\alpha]_{5461}^{20} -25.73^\circ$ in COMe_2 , and mixed 3-methylcyclohexan-1-ol-1-carboxylic acids the *Me* esters (I) of which have b.p. $98-99/16$ mm., $[\alpha]_{5786}^{20} +29.73^\circ$, $[\alpha]_{5461}^{20} +34.17^\circ$, $[\alpha]_{4358}^{20} +62.12^\circ$, and b.p. $108/16$ mm., $[\alpha]_{5786}^{20} -7.93^\circ$, $[\alpha]_{5461}^{20} -8.52^\circ$, $[\alpha]_{4358}^{20} -14.27^\circ$, respectively. 1-(I) with $\text{NH}_3\text{-EtOH}$ yields the *amide*, m.p. 128° , $[\alpha]_{5461}^{20} -2.28^\circ$, $[\alpha]_{4358}^{20} -4.19^\circ$ in COMe_2 , from which is obtained the *acid*, m.p. $97-98^\circ$, $[\alpha]_{5461}^{20} -6.60^\circ$, $[\alpha]_{4358}^{20} -11.01^\circ$ in COMe_2 (*anilide*, m.p. 109° , $[\alpha]_{\text{D}}^{20} -11.5^\circ$ in C_6H_6). F. N. W.

Brominated sterol ketones. A. BUTENANDT, G. SCHRAMM, A. WOLFF, and H. KUDSZUS (Ber., 1936, 69, [B], 2779—2783).—Cholestanone with Br (1 mol.) gives 2-bromocholestanone (I), transformed by further bromination into a Br_2 -compound, m.p. $193-194^\circ$, also obtained from (I). Contrary to Ruzicka *et al.* (A., 1936, 1382) this is regarded as 2:4-dibromocholestanone, since it is transformed by KOAc in BuOH into cholestane-3:4-dione (II), m.p. $147-148^\circ$, characterised by marked absorption at $280 \text{ m}\mu$, the formation



of a dark red colour with FeCl_3 , and the formation of a *mono-enol acetate*, m.p. $100-101^\circ$, which shows strong absorption between 240 and $250 \text{ m}\mu$. The *quinoxaline* derivative has m.p. $207-208^\circ$. The constitution of (II) follows further from its ready oxidation by H_2O_2 to the dihydro-Diels acid (III). Further, cholesterol hydrochloride is oxidised by CrO_3 to 5-chlorocholestanone, m.p. 102° or 135° (according as solvent of crystallisation is present or not), which with Br gives 5-chloro-4-bromocholestanone (IV), m.p. 122° , whence an $\alpha\beta$ -unsaturated Br_1 -ketone, m.p. 123° . (IV) with KOAc and AcOH gives (II) and cholestane-3:6-dione which is compatible only with the presence of the halogens at 4 and 5 in (IV).



Dibromocoprostanone, m.p. $135-136^\circ$ [Ruzicka (*loc. cit.*) gives m.p. 143°], is obtainable from 4-bromocoprostanone and its quinoxaline derivative is identical with that derived from (II). It is probably but not certainly (V).

Bromination of Δ^4 -cholestenone (VI) under varied conditions gives a variety of products among which is a dibromide, m.p. 177° , or, occasionally, m.p. 183° , apparently identical with the 2:4-dibromo- Δ^4 -cholestenone of Ruzicka (*loc. cit.*). This is regarded as (VII) for the following reasons. The absorption

spectrum is similar to that of cholestenedione Et ether and indicates double conjugation to CO . (VII) is obtained by direct bromination of (VI) or from the saturated tribromide $\text{C}_{27}\text{H}_{41}\text{OBr}_3$, m.p. about $182-183^\circ$, obtained by bromination of (VI) in presence of KOAc and readily converted by loss of HBr into (VII) thus establishing the empirical formula and degree of unsaturation. Further the Br_4 -ketone (VIII), m.p. 128° , passes readily by loss of HBr into the $\alpha\beta$ -unsaturated Br_3 -ketone, m.p. 165° , which by further loss of HBr gives (VII) in good yield, also obtainable directly from (VIII). Br is therefore at $\text{C}_{(4)}$ and $\text{C}_{(6)}$ not at $\text{C}_{(2)}$, and the doubly unsaturated character is confirmed. Other products of the bromination of (VI) are a doubly unsaturated Br_3 -ketone, $\text{C}_{27}\text{H}_{39}\text{OBr}_3$, m.p. $165-166^\circ$, $[\alpha]_{\text{D}}^{20} -22^\circ$, absorption max. at $313 \text{ m}\mu$, and a trebly unsaturated Br_2 -ketone, m.p. 203° , $[\alpha]_{\text{D}}^{20} -38^\circ$ (*oxime*, m.p. 118°). H. W.

Sterol-œstrone group. I. Synthesis of 3-keto-3:4-dihydro-1:2-cyclopentenophenanthrene. J. C. BARDHAN (J.C.S., 1936, 1848—1851).— $\text{CHNaAc}\cdot\text{CO}_2\text{Me}$ and $\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{COCl}$ in Et_2O give *Me* γ -diketo-8-carbomethoxyheptate, b.p. $137/0.5$ mm., which with cold $\text{NH}_3\text{-Et}_2\text{O}$ gives a good yield of *Me* β -ketoadipate (I), b.p. $122/0.5$ mm. $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ leads similarly to *Me* γ -diketo-8-carbethoxyheptate, b.p. $136/0.6$ mm., and *Me* *Et* β -ketoadipate, b.p. $123/0.5$ mm. (I) with hot dil. HCl gives lœvulic acid, but with cold conc. HCl affords β -ketoadipic acid in good yield; this is remarkably stable. (I), NaOMe, and $\beta\text{-l-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ give *Me* γ -keto-8-carbomethoxy- ζ -1-naphthylheptate, b.p. about 195° (slight decomp.) 0.5 mm., which with cold H_2SO_4 gives an ester, hydrolysed (KOH-MeOH) to 2-carboxy-3:4-dihydrophenanthrene-1- β -propionic acid, m.p. $237-238^\circ$ (*Me* ester, m.p. 75°); with Ac_2O at $155-210^\circ$, this gives 3'-keto-3:4-dihydro-1:2-cyclopentenophenanthrene, m.p. 210° (*semicarbazone*, m.p. $>285^\circ$), which, when reduced (Zn-Hg) and then dehydrogenated (Se at $310-330^\circ$), affords 1:2-cyclopentenophenanthrene. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$ and (I) give *Me* γ -keto-8-carbomethoxy- ζ -phenylheptate, b.p. $185/1$ mm., which with NaOMe and MeI gives *Me* γ -keto-8-carbomethoxy- ζ -phenyl- δ -methylheptate, b.p. $189/1$ mm. (œstrone *Me* ether (II), HCO_2Et , and Na in C_6H_6 give the *formyl* derivative, m.p. $170-171^\circ$, the *oxime* of which with 33% KOH gives 2-carboxy-7-methoxy-2-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-1- β -propionic acid, m.p. $251-252^\circ$, which with Ac_2O regenerates only (II) and with Se gives a cryst. hydrocarbon. R. S. C.

Ketonic derivatives of acetylbenzoyl. K. von AUWERS and H. LUDEWIG (Annalen, 1936, 526, 130—143).—All ketonic reagents appear to attack first the aliphatic half of the AcBz mol. This appears to be true for homologous aliphatic-aromatic α -diketones unless exception is caused by very marked branching of the aliphatic chain. For derivatives of AcBz it is proposed to use A and B according as substitution occurs at the aliphatic or benzenoid portion of the mol. Acetylbenzoyloxime-A (I), m.p. $114-115^\circ$, is readily obtained from CPhEt, isoamyl nitrite, and HCl. The corresponding oxime

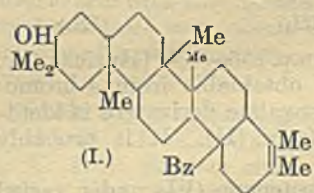
B (II), m.p. 166—167°, is not readily prepared from $\text{CH}_2\text{Ph}\cdot\text{COMe}$ and is best derived from $\text{CMe}_2\text{N}\cdot\text{OH}$ and PhN_2Cl in acid solution. Both isomerides are readily converted into the dioxime, m.p. about 235° when rapidly heated. AcBz and $\text{NHPh}\cdot\text{NH}_2$ in EtOH afford *acetylbenzoylphenylhydrazone-A* (III), m.p. 144—145°, the structure of which is confirmed by its production from PhN_2Cl and the product of the alkaline hydrolysis of $\text{CHMeBz}\cdot\text{CO}_2\text{Et}$ or from PhN_2Cl and $\text{OH}\cdot\text{CH}\cdot\text{CEtBz}$. Analogous methods lead to the corresponding *p*-nitrophenylhydrazone-A, m.p. 217—219° or m.p. 221° according to the mode of heating, and the 2:4-dinitrophenylhydrazone-A, m.p. 18·7° [accompanied by an orange-yellow (?) variety and the osazone, $\text{C}_{11}\text{H}_{10}\text{O}_8\text{N}_8$, m.p. 257°]. *Hydroxy-methylenebenzyl Me ketone*, m.p. 73—74°, from $\text{CH}_2\text{Ph}\cdot\text{COMe}$ and HCO_2Et , and PhN_2Cl afford *acetylbenzoylphenylhydrazone-B* (IV), m.p. 124—125°. (I) and $\text{NHPh}\cdot\text{NH}_2$ in EtOH afford *acetylbenzoylphenylhydrazone-B-oxime-A*, m.p. 207° (acetate, m.p. 136°), also obtained from (IV) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in presence or absence of alkali or, as abnormal product, from (III) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in boiling EtOH , whereby a substance, $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$, is also produced. Attempts to prepare a hydrazoneoxime from (II) were unsuccessful. The monosemicarbazone-A (V), m.p. 208—209°, is converted by NH_2OH into the *semicarbazone-A-oxime-B*, m.p. 203° (decomp.) according to the rate of heating, also obtained from (II), $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ and NaOAc in $\text{EtO}-\text{H}_2\text{O}$ at 40—50°; application of the latter method to (I) leads to the *semicarbazone-B-oxime-A*, decomp. 217—218° after becoming discoloured at 210°. (V) and $\text{NHPh}\cdot\text{NH}_2$ in warm EtOH yield the *semicarbazone-A-phenylhydrazone-B*, m.p. 194—196° (decomp.), also derived from (IV) and $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, whilst the *semicarbazone-B-phenylhydrazone-A*, decomp. 228—229° after becoming discoloured at 225°, is obtained from (III). H. W.

$\alpha\beta$ -Ketols. K. VON AUWERS, H. LUDEWIG, and A. MÜLLER (Annalen, 1936, 526, 143—172).—The optical behaviour of the supposed $\text{OH}\cdot\text{CHMeBz}$ (ketol-B), obtained by conversion of CHBrMeBz into $\text{OAc}\cdot\text{CHMeBz}$ and hydrolysis of the latter with boiling H_2O containing BaCO_3 , is traced to unchanged acetate. Prolonged hydrolysis, whether in quartz or SiO_2 , leads mainly to $\text{CHPhAc}\cdot\text{OH}$ (ketol-A) (I). Treatment of the mixture with aq. NaHSO_3 has little effect on the optical properties of the dissolved portion and leaves only a small residue. The process cannot be applied preparatively, since NaHSO_3 unites with both ketones. Homogeneous (I) is obtained from $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}_2$ and MgMeI but much by-product is formed. Pure *benzoylmethylcarbinol* (II), b.p. 123°/14 mm., is not easily obtained from $\text{COPh}\cdot\text{CHO}$ and MgMeI and is best prepared from $\text{COPh}\cdot\text{CHMeBr}$ and HCO_2K in boiling MeOH . (I) and (II) are yellow liquids which reduce cold Fehling's solution. When treated successively with PCl_3 and $\text{Zn} + \text{AcOH}$ (I) and (II) give $\text{COMe}\cdot\text{CH}_2\text{Ph}$ and COPhEt , respectively. (II) can be distilled unchanged under 14 mm., but becomes partly isomerised at its b.p./atm. pressure; prolonged boiling with $\text{H}_2\text{O}-\text{BaCO}_3$ converts it almost completely into

(I). It is more stable towards acid, but hydrolysis of its acetate by H_2SO_4 gives mainly (I). Indications of the reverse change are not obtained apart from processes of esterification. The *oxime* of (II) has m.p. 133—134°, and that of (I) m.p. 112·5°. (II) is transformed by $\text{NHPh}\cdot\text{NH}_2$ into *acetylbenzoylphenylhydrazone-A*, m.p. 144—145°, whereas (I) yields only non-cryst. products. (I) gives a 2:4-dinitrophenylhydrazone (III), m.p. 126°, the constitution of which is confirmed by the formation of an acetate, m.p. 165—166°, and by its non-identity with *acetylbenzoyldinitrophenylhydrazone*; the structure of Hey's product, m.p. 170° (A., 1930, 935), is unexplained. In cold EtOH (II) and 2:4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}\cdot\text{NH}_2$ react very slowly, whereas in boiling EtOH (III) is produced; in AcOH at room temp. the product is *s*-acetyldinitrophenylhydrazine. (I) gives the corresponding *semicarbazone* characterised by oxidation to *acetylbenzoylsemicarbazone-A*. (II) reacts slowly with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ giving exclusively *acetylbenzoyldisemicarbazone* (II), m.p. about 240°, the production of which is never observed from (I) and is a certain sign of the presence of (II) in mixtures. Unexpectedly, (IV) is also derived from $\text{COPh}\cdot\text{CHMeBr}$ and $\text{COPh}\cdot\text{CHMe}\cdot\text{OAc}$. Treatment of (I) or (II) with MgMeI leads to mixtures of $\text{OH}\cdot\text{CPhMe}\cdot\text{CHMe}\cdot\text{OH}$ and $\text{OH}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{OH}$ in varying proportion, partial isomerisation of (I) taking place. With MgPhBr reaction is more orderly, $(\cdot\text{CPhMe}\cdot\text{OH})_2$ being obtained from (I) and $\text{OH}\cdot\text{CPh}_2\cdot\text{CHMe}\cdot\text{OH}$ from (II). (I), Ag_2O , and MeI afford the corresponding *Me ether*, b.p. 107—108°/15 mm. (*semicarbazone*, m.p. 157·5—158·5°). (I) with boiling Ac_2O yields an incompletely homogeneous material, b.p. 136—140°/11 mm., the physical consts. of which show it to be derived mainly from (II). Benzoylation appears to be accompanied by a somewhat less pronounced isomerisation of (I) into (II). (II) and PhNCO unite rapidly to the phenylurethane, $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CHMeBz}$, m.p. 144—145°, also obtained slowly and accompanied by $\text{CO}(\text{NHPh})_2$ from (I). The transformations do not appear to occur through definite intermediate products, but, as with desmotropic compounds, to be due to the wandering of H atoms or radicals.

H. W.

Phenyl acetyloleanyl ketone. H. GRASSHOF and E. WEDEKIND (Ber., 1936, 69, [B], 2686—2688).—*Me oleanolate* does not react with Grignard's reagents even in boiling PhMe . *Acetyloleanoic acid* is transformed by SOCl_2 into the corresponding *chloride*, transformed by MgPhBr in Et_2O and subsequent treatment with boiling Ac_2O into *Ph acetyloleanyl ketone*, m.p. 234—235°, hydro-



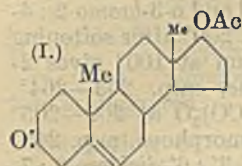
Grignard product by CrO_3 in boiling AcOH .

H. W.

Δ^5 -Androsten-17-ol-3-one, an isomeride of testosterone. A. BUTENANDT and G. HANISCH (Ber., 1936, 69, [B], 2773—2775).—*Androstene-3:17-*

lysed by boiling $\text{KOH}-\text{MeOH}$ to *Ph oleanyl ketone* (I), m.p. 234—235°. Behenic acid is isolated in small amount from the products of the oxidation of the crude

diol 17-acetate is brominated in AcOH and then cautiously oxidised by CrO_3 to the Br_2 -ketone, which is converted by Zn dust in boiling MeOH into



Δ^5 -androsten-17-ol-3-one-17-yl acetate, (I), m.p. 147° after softening at 130° , $[\alpha]_D^{20} -30.5^\circ$ in EtOH, and a substance, $\text{C}_{22}\text{H}_{30}\text{O}_4$ (? Me ether), m.p. 180° after softening at $165-170^\circ$. Attempts to hydrolyse (I) to the corresponding alcohol were unsuccessful on account of the ready displacement of the double linking towards Δ^4 . It is isomerised by HCl in MeOH to testosterone acetate (II). Physiologically (I) is considerably more active than (II). H. W.

Simple preparation of the chloroketone $\text{C}_{19}\text{H}_{27}\text{OCl}$ (dehydroandrosteryl chloride) isolated from male urine. A. BUTENANDT and W. GROSSE (Ber., 1936, 69, [B], 2776—2778).—Dehydroandrosterone is converted by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ into its *p*-toluenesulphonate, m.p. $157-158^\circ$, $[\alpha]_D^{20} -12.1^\circ$ in dioxan, transformed by boiling MeOH into *dehydroandrosterone Me ether*, m.p. $140-142^\circ$, $[\alpha] \pm 0^\circ$ in CHCl_3 , and by KOAc in boiling MeOH into *epidehydroandrosterone Me ether* (I), b.p. $100-110^\circ/0.001\text{ mm.}$, $[\alpha]_D^{20} +111^\circ$ in CHCl_3 . (I) is smoothly transformed by conc. HCl in AcOH into *dehydroandrosteryl chloride* [3-chloro- Δ^5 -aetiocholen-17-one], m.p. $155-157^\circ$, $[\alpha]_D^{20} +14^\circ$ in CHCl_3 , identical with the substance isolated from male urine. H. W.

Sex hormones. XVIII. Preparation of further enol-esters from ketones of the cholestane and androstene series. L. RUZICKA and W. F. FISCHER. XIX. Preparation of Δ^5 -3-epihydroxyandrosten-17-one (Δ^5 -epidehydroandrosterone). L. RUZICKA and M. W. GOLDBERG (Helv. Chim. Acta, 1936, 19, 1371—1375, 1407—1410; cf. A., 1936, 1382).—XVIII. The following enolic esters are prepared: *cholestanone benzoate*, m.p. $127-128^\circ$, Δ^4 -androstene-3:17-dione acetate (I), m.p. $127-129^\circ$, and *testosterone di-benzoate*, m.p. $183-184^\circ$ (decomp.), -acetate (II), m.p. $150-151^\circ$, and -propionate, m.p. $127-219^\circ$. [E. TSCHOPP.] (I) and the corresponding benzoate and (II) have powerful male, but no female, sex hormone activity.

XIX. Partial hydrogenation (Raney Ni) of Δ^5 -cholestenone in cyclohexane gives a mixture of cholesterol and epicholesterol, m.p. 141° , $[\alpha]_D -37.5^\circ$ in EtOH (acetate, m.p. 85°). Δ^5 -Androstenedione gives similarly *trans*- and *epi*-hydroxyandrosten-17-one, m.p. 221° , sublimes at $140^\circ/0.01\text{ mm.}$, $\alpha 0$ in EtOH (acetate, m.p. $173.5-174.5^\circ$; oxime, m.p. $204-206^\circ$). M.p. are corr. R. S. C.

Halogenation of phenolic ethers and anilides. VIII. Alkoxy- and dialkoxy-benzophenones and dialkoxydiphenylsulphones. B. JONES (J.C.S., 1936, 1854—1862).—*pp'*-Dihydroxydiphenyl sulphoxide, m.p. 194° , with AcOH and H_2O_2 gave the sulphone, m.p. 239° , which with NaOEt and alkyl bromide gave the following 4:4'-dialkoxydiphenylsulphones: *n*- and *iso*-dipropoxy-, m.p. $142-143^\circ$ and 157° , respectively, *di-n*-butoxy-, m.p. 92.5° , and *di-n*-amyl-, m.p. 86.5° . The following benzophenones were prepared: *pp'*-*di-n*-propoxy-, m.p. 127° , *pp'*-*di*-iso-

propoxy-, m.p. 72.5° , *pp'*-*di-n*-butoxy-, m.p. 118° , *pp'*-*di-n*-amyl-, m.p. 108° , *p*-methoxy-*p'*-ethoxy-, m.p. 111° , *p*-methoxy-*p'*-*n*-butoxy-, m.p. $105-106^\circ$, *p*-methoxy-*p'*-*n*-amyl-, m.p. 101° , *p*-methoxy-*p'*- β -chloroethoxy-, m.p. 106° , *p*-ethoxy-*p'*-*n*-butoxy-, m.p. 103° , *p*-ethoxy-*p'*-*n*-amyl-, m.p. 95° , 3'-chloro-4-methoxy-4'-ethoxy-, m.p. 108° ; 3'-chloro-4:4'-dimethoxy-, m.p. 97.5° , 3'-chloro-4-methoxy-4'-*n*-propoxy-, m.p. 77° , *p-n*-butoxy-, m.p. 37° , *p-n*-amyl-, m.p. 41° , *p-n*-heptyloxy-, m.p. 47° , 2'-, 3'-, and 4'-fluoro-4-methoxy-, m.p. 49° , 72° , and 95° , respectively, 2'- and 4'-chloro-4-methoxy-, m.p. 80° and 125.5° , respectively, 4'-chloro-4-ethoxy-, m.p. 121° , 2'-chloro-4- β -chloroethoxy-, m.p. 65° , 3'- and 4'-bromo-4-methoxy-, m.p. 80° and 154° , respectively, 4-methoxy-3'- and 4'-methyl-, m.p. 56° and $90-91^\circ$, respectively, 3'-nitro-4-methoxy-, m.p. 93° , and 3'-nitro-4-*n*-butoxy-, m.p. 73° .

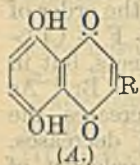
The velocities of chlorination were determined in 99% AcOH at 20° . In the series of symmetrical benzophenones (I) and diphenylsulphones (II) the same relative directive powers for the alkoxy-groups are found as for the simpler ethers $\text{RO}\cdot\text{C}_6\text{H}_4\cdot\text{X}$ (cf. A., 1936, 719) and the reactivities of analogous (I) and (II) are in the ratio $100:2.38$. For polar groups X in ketones of the type $p\text{-RO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{X}$ the order of reactivity for *p*-substituents is $\text{Me} > \text{H} > \text{F} > \text{Cl} > \text{Br} > \text{NO}_2$; *m*-F and Br have identical effects, but in the *o*-position the order of reactivity is $\text{F} > \text{Br}$. As the strength of the acid $\text{C}_6\text{H}_4\text{X}\cdot\text{CO}_2\text{H}$ increases, the reactivity of the corresponding ketone decreases. *p*-Alkoxybenzophenones, in respect of velocity of chlorination, are 2.87 times as reactive as the corresponding *p*-alkoxybenzoic acids. J. G. A. G.

Cyclitol series. IV. Inosose, a cyclose derivative of mesoinositol. T. POSTERNAK (Helv. Chim. Acta, 1936, 19, 1333—1345; cf. A., 1936, 1376).—A "cyclose" (ketose with an isocyclic ring) is prepared and shown to have a free CO. It is converted in stages into phloroglucinol (I), a conversion which may have biogenetic significance. *meso*Inositol and HNO_3 (*d* 1.4) give inosose (II) (2:3:4:5:6-pentahydroxycyclohexanone), m.p. $198-200^\circ$ [phenyl-, m.p. $220-222^\circ$ (block), and 2:4-dinitrophenyl-hydrazone, m.p. 270° (block); semicarbazone, decomp. 207° ; no osazone]. NaOBr gives, much less well, a similar compound (phenylhydrazone, m.p. $192-194^\circ$). (II) reduces cold Fehling's solution and $\text{AgNO}_3\text{-NH}_3$ at once and consumes 2 equivs. of alkaline NaOH. With $\text{Ac}_2\text{O-H}_2\text{SO}_4$ (little) (II) gives an Ac_5 (III), m.p. $106-108^\circ$, and with BzCl-ZnCl_2 at $110-130^\circ$ a Bz_5 derivative (IV), m.p. 144° . The acyl derivatives are very sensitive to weak bases; e.g., (III) with NaOAc or $\text{C}_5\text{H}_5\text{N}$ gives 1:2:3:5-tetra-acetoxybenzene (V), m.p. $107-108^\circ$, which is also formed on attempted acetylation in presence of NaOAc or $\text{C}_5\text{H}_5\text{N}$. Hydrogenation (PtO_2) of (III) in abs. EtOH yields epinositol penta-acetate, m.p. $153-154^\circ$ ($\text{Ac}_2\text{O-ZnCl}_2$ gives the hexa-acetate, m.p. 188°), hydrolysed by Ba(OH)_2 in aq. MeOH to epinositol, decomp. about 285° (Bz_6 derivative, m.p. 224°), also obtained similarly or by Na-Hg from (II). (IV) in hot NaOAc-AcOH or, less well, in cold $\text{C}_5\text{H}_5\text{N}$ gives 2:3:5-tribenzoyloxyphenol, m.p. $167-168^\circ$ (no FeCl_3 colour; BzCl gives 2:3:4:5-tetrabenzoyloxybenzene, m.p.

118°), the *Me* ether, m.p. 134°, of which is obtained by CH_2N_2 or from 2-hydroxy-6-methoxybenzoquinone by reduction with $\text{Na}_2\text{S}_2\text{O}_4$, followed by benzylation. 1 : 2 : 3 : 5- $\text{C}_6\text{H}_2(\text{OH})_4$ or $\text{C}_6(\text{OH})_6$ with Na-Hg gives (I). R. S. C.

Oxidation of quinol by air in presence of methylammonium sulphite. Oxidation of quinolsulphonic acid in presence of methylamine. (MLLE.) Y. GARREAU (Compt. rend., 1936, 203, 1073—1074; cf. A., 1935, 338).—*Bismethylaminobenzoquinonesulphonic acid* (NH_2Me salt + $4\text{H}_2\text{O}$, decomp. 105°; *glycine* salt + H_2O , m.p. 235°) results from the action of air on a solution of quinolsulphonic acid in aq. NH_2Me in presence of $\text{Cu}(\text{OH})_2$, or on quinol and SO_2 in aq. NH_2Me in presence of $\text{Cu}(\text{OH})_2$. F. N. W.

Constitution of shikonin. Syntheses of *iso*-hexylnaphthazarin and related compounds. C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1936, 12, 239—241).—When heated with AlCl_3 + NaCl, *p*-anisyl isohexanoate affords 2 : 5-dihydroxyphenyl isomethyl ketone, m.p. 68.5°, reduced by Zn-Hg to 2-*isohexylquinol*, m.p. 100°, converted by heating with maleic anhydride- AlCl_3 -NaCl into *iso*-hexylnaphthazarin, m.p. 100° (*A*, $\text{R} = [\text{CH}_2]_2\cdot\text{CH}_2\text{Pr}^{\beta}$), identical with the product obtained by catalytic reduction of shikonin *Me* ether. By similar methods are prepared 2 : 5-dihydroxyphenyl Pr^{α} , m.p. 91°, and Bu^{β} , m.p. 111°, ketone, reduced to 2-*n*-butyl-, m.p. 86°, and 2-*isoamyl*-, m.p. 96°, -quinol, from which homologues of *A*, $\text{R} = \text{Et}$, m.p. 126°, Bu^{α} , m.p. 118° and $\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^{\alpha}$, m.p. 89°, are prepared. No details or analyses are given. J. W. B.



Effect of alkyl groups on the properties of anthraquinone and fluorescein dyes. R. M. HARRIS, G. J. MARRIOTT, and J. C. SMITH (J.C.S., 1936, 1838—1844).—Increasing the length of the alkyl group in 1-amino-2-alkylantraquinones lowers the m.p., shifts and broadens the absorption band slightly, increases the extinction coeff., and, up to Bu rapidly and thereafter slowly, the general absorption. A similar change in Na 1-amino-4-anilino-2-alkylantraquinone-*p*-sulphonates causes less marked changes in the absorption, but increases the rate of dyeing and, up to C_7 , the covering power on wool. Alkyl groups in fluorescein dyes probably increase the absorption of red light and the covering power. Prep. of the following is described. 1-Amino-2-methylantraquinone; PhBu^{α} , *o*-*p*'-*n*-butyl-benzoyl-, m.p. 99°, and (by Zn-Cu- NH_3)-benzyl-benzoic acid, m.p. 86°, 2-*n*-butylantraquinone, m.p. 87.5° (1- NO_2 -, m.p. 147.5°, and 1- NH_2 -derivatives, m.p. 174—175°); $\text{COPh}\cdot\text{C}_6\text{H}_{13}$, b.p. 140—150°/15 mm., m.p. 17°, *n*- $\text{C}_7\text{H}_{15}\text{Ph}$, *o*-*p*-*n*-heptyl-benzoyl-, m.p. 99—101°, and -benzyl-benzoic acid, m.p. 69—71°, b.p. 220°/0.2 mm., 2-*n*-heptylantraquinone, m.p. 76° (1- NO_2 -, m.p. 137°, and 1- NH_2 -derivative, m.p. 138—139°); 1-amino-2-*n*-dodecylantraquinone, m.p. 134—135°. 1-Amino-4-anilino-2-methylantraquinone, m.p. 245.5°, is obtained from the 4-Br-compound, KOAc , $\text{Cu}(\text{OAc})_2$, and NH_2Ph at 160°, and with oleum affords the *Na* *p*'-sulphonate; the 2-*n*-heptyl- and 2-*n*-dodecyl-dyes are

also prepared. 3 : 6-Dichlorofluorescein has m.p. 285—286°. The structure of 4 : 5-dibromofluorescein, m.p. 283°, is confirmed by degradation by 50% NaOH at 120—130° to 2-bromoresorcinol and *o*-3-bromo-2 : 4-dihydroxybenzoylbenzoic acid, m.p. 200° after softening at 187°, which with H_3BO_3 -oleum at 100° gives 2-bromo-1 : 3-dihydroxyanthraquinone, m.p. 263—264°. 4-*n*-Hexylresorcinol and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ at 200—205° give 2 : 7-di-*n*-hexylfluorescein, dimorphous, m.p. 245° (4 : 5- Br_2 -derivative, m.p. 188°); 3' : 6'-dichloro-2 : 7-di-*n*-hexylfluorescein, m.p. 228—229° (4 : 5- Br_2 -derivative, m.p. 169—170°), is also prepared. R. S. C.

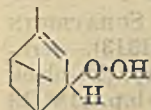
Intermediate products in dehydrogenations with quinones. R. CRIGGEE (Ber., 1936, 69, [B], 2758—2761).—Dichloroquinizarinquinone (I) and 1 : 2 : 3 : 4-tetrahydronaphthalene at 100° yield tetrahydronaphthyl dichloroquinizarin ether (II), in which the presence of OH is proved by Zerevitinov's method and by the production of the acetate (III), m.p. 160° (decomp.). (II) at 140—170° gives dichloroquinizarin (IV) and Δ^1 -dihydronaphthalene (V). At 150°, (III) is decomposed into (V) and dichloroquinizarin monoacetate, m.p. 209—211°, thus showing that an initial decomp. into the parent substances does not occur. (I) and cyclohexene at 125—135° afford cyclohexenyl dichloroquinizarinyl ether [*Ac* derivative, m.p. 130—132° (corr.; gradual decomp.)], which at 180—190° passes into (IV) and $\Delta^{1,3}$ -cyclohexadiene. During dehydrogenations, therefore, quinones do not invariably behave solely as acceptors, but may yield main valency, additive products with the substrate. H. W.

Influence of solvent on the course of chemical reactions. IX. Kinetics of simple substitution reactions.—See A., I, 87.

Phellandrenes. IV. Comparison of the catalytic dehydrogenation of *l*- α -phellandrene and *l*-piperitone. J. DEWAR and J. READ (J.C.S., 1936, 1781—1783).—Piperitone was practically unaffected by Pt-asbestos, Pt-C, or Pd-C at 300°, but it was converted almost quantitatively into thymol by Zelinski's Pt-C (CO_2 ; 300°). Rupe's porcelain-Ni catalyst similarly effected conversion (70%) into thymol at 250°, and at room temp. in H_2 , piperitone was hydrogenated to menthones. *l*- α -Phellandrene, with an activated Ni catalyst in CO_2 , gave a mixture (4 : 1) of *p*-cymene and *p*-menthane. F. R. S.

Synthesis of *trans*-*s*-homopinic acid. P. C. GUHA and K. GANAPATHI (Current Sci., 1936, 5, 244).—Reduction of either *cis*- or *trans*-Et norpinate with Na-abs. EtOH gives the *trans*-diol, the dibromide, b.p. 100—102°/4 mm., of which is converted by boiling NaCN -EtOH into the dinitrile, b.p. 142—145°/6 mm., hydrolysed by boiling 20% KOH to *trans*-2 : 2-dimethylcyclobutane-1 : 3-diacetic acid (*trans*-*s*-homopinic acid), m.p. 120—121° (dianilide, m.p. 219—220°; Et_2 ester, b.p. 131—132°/4 mm.), stable to distillation over $\text{Ba}(\text{OH})_2$ and converted by Ac_2O only into the double anhydride. J. W. B.

Pinene peroxide. K. SUSUKI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 70—71).—The α -pinene peroxide, d_{44}^{25} 0.9810, n_D^{25} 1.4885, $[\alpha]_D^{25}$ +21.22°, obtained by autooxidation of d - α -pinene, with H_2 -PtO₂ gives some dihydroverbenol and with KMnO₄ pinonic acid. The annexed structure is suggested. R. S. C.



Oxidation of α -pinene with potassium permanganate in acetone solution. T. KUWATA (J. Soc. Chem. Ind. Japan, 1936, 39, 394—395B).— d - α -Pinene (I) in 90% aq. COMe₂ containing KMnO₄ [2 O to 1 mol. of (I)] at 10—15° affords d - α -pinonic acid, m.p. 101—103°, and (d)-1-hydroxy-6-keto-1:3:3-trimethyl-2:4-methylenecyclohexane, m.p. 35.5—36.5° [semicarbazone, m.p. about 230° (decomp.)]. J. L. D.

Catalytic action of Japanese acid clay on terpene compounds. V. Hydration of α -pinene with acetic acid. T. KUWATA (J. Soc. Chem. Ind. Japan, 1936, 39, 392—394B).— α -Pinene with AcOH containing Ac₂O and clay free from acid-sol. material affords d -limonene (I), bornyl, isobornyl, and terpinyl acetate, the last probably formed from (I).

J. L. D.

Terpene compounds. III. Synthesis of isofenchocamphononic acid. J. C. BARDHAN and N. C. GANGULY (J.C.S., 1936, 1852—1853).—Et α -dimethyl-lavulate and CN·CH₂·CO₂Et with C₅H₁₁N give *Et* α -cyano- β δ -dimethyl- Δ^2 -pentene- α δ -dicarboxylate, b.p. 165°/4 mm., which with KCN yields the *Et* ester (I), b.p. 161°/4 mm., of β δ -dimethylpentane- α β δ -tricarboxylic acid, m.p. 200—201° (ester-imide, m.p. 88—89°). (I) with Na in C₆H₆ affords *Et* 2:2:4-trimethylcyclopentan-1-one-4:5-dicarboxylate, b.p. 135°/4 mm., hydrolysed to 2:2:4-trimethylcyclopentan-1-one-4-carboxylic acid, m.p. 70—71° (*Et* ester, b.p. 96—97°/3 mm., and its semicarbazone, m.p. 180—181°), which must be identical with Aschan's isofenchocamphononic acid. F. R. S.

Racemisation in the camphene rearrangement. A. I. SCHAVRIGIN (J. Gen. Chem. Russ., 1936, 6, 1314—1324).—*tert*-Methylfenchyl alcohol, $[\alpha]_D$ +9.04°, yields α -methylcamphene, $[\alpha]_D$ +14.87° to +31.85° in Et₂O, depending on the duration of heating with anhyd. K₂CO₃ or NaHSO₄, and this affords 4-methylisobornyl acetate (I), $[\alpha]_D$ +15.1°, from which 4-methylisoborneol (II), $[\alpha]_D$ +9.84°, is obtained by hydrolysis. This is converted by heating with NaHSO₄ into β -methylcamphene, $[\alpha]_D$ -6.45°, from which (I), $[\alpha]_D$ +4.21°, and (II), $[\alpha]_D$ +3.72°, are obtained as above. The camphene rearrangement of type I involves inversion of optical rotation in passing from camphene to isoborneol, or *vice versa*, whilst type II involves two successive inversions, yielding a final product with optical rotation of the same sign as the initial product. A no. of schemes explaining the structural rearrangements involved are given. All $[\alpha]_D$ are in EtOH except where stated otherwise.

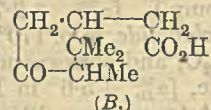
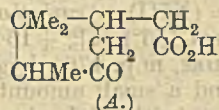
R. T.

Total synthesis of camphenilone and of α - and β -fenchocamphorone. G. KOMPPA and O. KOMPPA (Ber., 1936, 69, [B], 2606—2610).—CMe₂·CH·CO₂H is converted by protracted boiling with an excess of

dicyclopentadiene into 3:3-dimethyltricyclo-[1:2:2]- Δ^5 -heptene-2-carboxylic acid, b.p. 141—141.5°/12 mm., hydrogenated (Pd) to isocamphenilanic acid (I), m.p. 115—116°. (I) is transformed through the chloride and azide essentially into camphenilamine; the alcohol obtained from this is a mixture oxidised by KMnO₄ to camphenilone, apocamphoric and *cis*-apocamphoric acid. The intermediate formation of apocycloene is assumed. H. W.

Stereoisomeric camphenilols. W. HÜCKEL and W. TAPPE (Ber., 1936, 69, [B], 2769—2772).—Camphene, b.p. 157.8°/742 mm., m.p. 49°, $[\alpha]_D$ -95.7°, from Siberian pine-needle oil, is oxidised to camphenilone (I), b.p. 193°/760 mm., m.p. 39°, $[\alpha]_D$ -60.8° in C₆H₆, reduced by Na and EtOH to camphenilol I, m.p. 76—77°, $[\alpha]_D^{20}$ -23.0° in EtOH (*H* phthalate, m.p. 146—147°, $[\alpha]_D^{20}$ -72.9° in C₆H₆; *p*-nitrobenzoate, m.p. 96—98°, $[\alpha]_D^{20}$ -42.1° in C₆H₆; *p*-aminobenzoate, m.p. 169°, $[\alpha]_D^{20}$ -60.4° in EtOH). Hydrogenation (Pt-sponge in AcOH saturated with HCl) of (I) leads (after purification) to camphenilol II, m.p. 98—101°, $[\alpha]_D^{20}$ +33.3° in EtOH (*p*-aminobenzoate, m.p. 161°, $[\alpha]_D^{20}$ +34.6° in EtOH). Alkaline or catalytic reduction of *r*-campheniloneoxime gives a mixture of *r*-camphenilamines one of which yields *Bz* and *Ac* derivatives, m.p. 149—151° and 135—136°, respectively, whereas the other affords *Bz* and *Ac* compounds, m.p. 104° and m.p. 99—100°, respectively. H. W.

Supposed transition of camphor or campholenic acid into pinonic acid. Dehydration of dihydroxydihydro- α -campholenic acid. G. KOMPPA and S. BECKMANN (Ber., 1936, 69, [B], 2783—2789).—Repetition of Tiemann's work on the oxidation of campholenic acid shows that the amount of oily by-products (I) can be greatly suppressed by suitable choice of conditions and that dl-dihydroxydihydro- α -campholenic acid (II), m.p. 138—139°, is readily isolated. α -Campholenic acid [Tiemann's "pinonic acid" (III)] is not present in (I) and is a product of the dehydration of (II), which occurs partly when it is distilled under diminished pressure or, more completely, under atm. pressure. Under these conditions the distillate is a mixture of dl- α -campholenic acid (IV), b.p. 186°/9 mm. [semicarbazone (V), m.p. about 240° (decomp.) according to the rate of heating; oxime, m.p. 188°], and 2:6-diketocamphane (V), m.p. 189—190° [dioxime, m.p. 244—245°; semicarbazone, m.p. 290° (decomp.)]. (II) is converted into (IV) by boiling dil. H₂SO₄. (IV) is transformed into (VI) when heated at its b.p. and (VI) into (IV) by boiling dil. HCl. Treatment of (V) with NaOEt-EtOH at 160—170° leads to dl- α -campholenic acid (corresponding amide, m.p. 124—125°). (IV) is therefore regarded as 2:3:3-trimethylcyclopentan-1-one-4-acetic acid and (III) is either *A* or *B*. The



reported formation (Tiemann) of pinic acid from (III) and NaOBr is erroneous. The formation of CHBr₃ or CBr₄ is due to impurities and the product

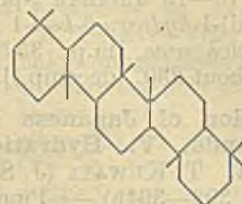
is a cryst. acid, $C_{10}H_{14}O_6$, m.p. 212—213°, or an optically active form, m.p. 229—230°, which can be neither identical nor isomeric with pinic acid. H. W.

Isomeric 2:3-diaminocamphanes. H. RUPE and P. BOHNY (Helv. Chim. Acta, 1936, 19, 1305—1323).—With Na-EtOH camphorquinonedioxime gives a mixture of α - (I) and an isomeric (II) 2:3-diaminocamphane; it resists H_2 -Ni, but with Al-Hg in Et_2O affords an isomeric β -diamine (III), which under acid conditions often gives derivatives of (I). (III), m.p. 148—149°, sublimes at 124°/12 mm., $[\alpha]_D^{20} +10.655^\circ$ in C_6H_6 , decomposes after some months in vac., gives a *mono-aurichloride*, decomp. 204—205°, *platinichloride*, decomp. 251°, $HgCl_2$ double salt, *thiocyanate*, *di-hydrochloride*, *cryst.*, *-perchlorate*, decomp. 267°, and *-picrate* (IV), m.p. 231° (decomp.), *oxalate*, m.p. 245°, *citrate*, decomp. 195°, *diurethane*, m.p. 139°, b.p. 158°/12 mm., Ac_2 (V) (no methylglyoxaline obtained), m.p. 307°, $[\alpha]_D^{20} +17.6^\circ$ in HCO_2H , Bz_2 (VI), m.p. 276° (a substance, $C_8H_{14} \begin{smallmatrix} CH \\ CH \end{smallmatrix} NBz$, m.p. 148°, is also formed), *di-p-nitrobenzoyl* (VII), m.p. 276°, *diphenylthiocarbamide* (VIII), m.p. 187°, *phenylcarbamide*, m.p. >260°, and *dicarbamide*, m.p. >280°, *di-p-nitrobenzylidene*, m.p. 170°, *-p-anisylidene*, an oil, and *-benzylidene*, b.p. 212°/12 mm., derivatives. With benzil and isatin (III) gives the substances (IX), $C_8H_{14} \begin{smallmatrix} CH-NR \\ CH-NR \end{smallmatrix}$, R = C(Ph)C(Ph), m.p. 19°, and $o-C_6H_4 \begin{smallmatrix} NH \\ C \end{smallmatrix} CO$ (X), decomp. 234°, $[\alpha]_D^{20} +9.2^\circ$ in dioxan. (III), Me_3SO_4 , and aq. NaOH give 7% of $NN'-Me_2$ (XI) [(NO)₂-derivative, m.p. 144—146°], and $NN'-Me_4$ derivative, b.p. 126°/11 mm., $d_4^{20} 0.9308$, $[\alpha]_D^{20} +29.22^\circ$ [*mono-picrate* (XII), m.p. 164° after sintering at 161°, *-methiodide* (XIII), decomp. 218°, $[\alpha]_D^{20} +3.3^\circ$ in 50% EtOH, *-carbethoxymethoperchlorate N'-perchlorate*, m.p. 170°, decomp. 208°, and *-carbethoxymethobromide*, m.p. 170° after sintering at 169° (with Ag_2O gives the *carboxymethobetaine*, m.p. 177°, $[\alpha]_D^{20} +10.665^\circ$ in H_2O); *diperchlorate*, decomp. 235°]. (I), b.p. 133—136°/12 mm., 246°/760 mm., and (II), b.p. 246°/760 mm., 125°/12 mm., are best separated by the Ac_2 derivatives, m.p. 308—309°, $[\alpha]_D^{20} +17.9^\circ$ in 80% HCO_2H [$? = (V)$], and m.p. 247.5—250°, $[\alpha]_D^{20} +19.5^\circ$ in 80% HCO_2H , respectively, which cannot be hydrolysed, or, less well, by way of the *oxalates*, m.p. 255° and 230°, respectively (a fraction, m.p. 275°, was also obtained). The crude mixture of (I) and (II), containing mostly (I), gives (VI), (VII), a *picrate*, m.p. 227—232° [$? = (IV)$], *diphenylthiocarbamide* derivative, m.p. 178—179° [$? = (VIII)$], and a substance (IX) [$R = (X)$], decomp. 194°, $[\alpha]_D^{20} -14.65^\circ$ in dioxan; with Me_2SO_4 it gives a little (XI) and much $NN'-Me_4$ derivative, b.p. 122°/12 mm., $[\alpha]_D^{20} +16.75^\circ$ [*picrate* = (XII); *methiodide*, m.p. 217° (decomp.), $[\alpha]_D^{20} +3.7^\circ$, $? = (XIII)$; *carbethoxymethobromide*, m.p. 170° (sinters at 155°), $[\alpha]_D^{20} +15.91^\circ$ in H_2O , and corresponding *betaine*, m.p. 176°, hygroscopic, $[\alpha]_D^{20} +5.6^\circ$ in H_2O], and a small amount of a substance, b.p. 165°/12 mm. (with MeI gives a substance, m.p. 96°, not a methiodide), which may be derived from (II). In both methylations some Me methosulphate, an oil, is obtained, which gives

the *methoperchlorate perchlorate*, decomp. 225°, also obtained from (XIII). R. S. C.

tert.-Propylfenchyl alcohol. A. I. SCHAVRIGIN (J. Gen. Chem. Russ., 1936, 6, 1310—1313).—*tert.*-Allylfenchyl alcohol and H_2 at room temp. (Pt-black catalyst) yield *tert.-propylfenchyl alcohol*, b.p. 118°/13 mm., from which a mixture of unsaturated hydrocarbons is obtained by heating with anhyd. $KHSO_4$ at 120°. R. T.

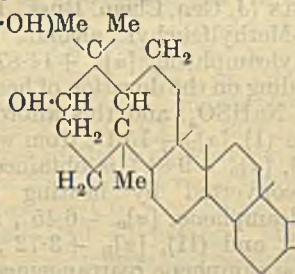
Structure of triterpenes. F. S. SPRING (Chem. and Ind., 1936, 1050—1051).—The annexed skeleton is adopted for triterpenes.



R. S. C.

Novel interrelationship in the triterpene group. J. H. BEYNON, I. M. HEILBRON, and F. S. SPRING (Nature, 1936, 138, 1017).—The alcohol previously described (A., 1934, 1330), now named *basseol*, is readily cyclised by various reagents to β -amyrin, furnishing the first example of the conversion of a naturally-occurring tetracyclic into a naturally-occurring bicyclic triterpene. L. S. T.

Polyterpenes and polyterpenoids. CVIII. Syntheses of the trimethylnaphthol obtained by dehydrogenation of pentacyclic terpenes. L. RUZICKA, K. HOFMANN, and H. SCHELLENBERG. CIX. Glycyrrhetic acid. L. RUZICKA and H. LEUBENBERGER (Helv. Chim. Acta, 1936, 19, 1391—1402, 1402—1405; cf. A., 1936, 1514).—CVIII. The Me_3 derivatives obtained by degradation of polyterpenes are 1:2:5- $C_{10}H_5Me_3$ and 2-methoxy-1:5:6-trimethylnaphthalene (I). Mixtures of styphnates, but not of picrates or $C_6H_5(NO_2)_3$ compounds, of isomeric $C_{10}H_5Me_3$ give definite depressions of the m.p. The structure of triterpenes and the general principles to be used for determination thereof are discussed. The annexed structure is suggested, only that part given in full having been confirmed by degradative experiments.



3:1:2- $OMe-C_6H_4Me-COMe$ [from the acid chloride (III) and $ZnMeI$], b.p. 131—132°/15 mm., with Mg (not Zn) and $CHMeBr-CO_2Et$ give *Et* β -hydroxy- β -6-methoxy- α -tolyl- α -methyl-*n*-butyrate, converted by successive dehydrogenation by I, hydrogenation (Pt; AcOH), and reduction by Na-EtOH into γ -6-methoxy- α -tolyl- β -methyl-*n*-butyl alcohol, b.p. 170—171°/15 mm.; the derived bromide, b.p. 160—162°/14 mm., gives, by way of the nitrile, γ -6-methoxy- α -tolyl- β -methylvaleric acid, m.p. 120—121°, the chloride (prep. by $SOCl_2-C_6H_6$) of which with $AlCl_3$ in CS_2 gives 1-keto-6-methoxy-3:4:5-trimethyl-1:2:3:4-

tetrahydronaphthalene. Clemmensen reduction at 50° followed by dehydrogenation (Pd-C) at 300° gives 2-methoxy-1 : 7 : 8-trimethylnaphthalene, m.p. 74—75° [1 : 3 : 5-C₆H₃(NO₂)₃ compound, m.p. 128—129°]. (II with CH₂N₂-Et₂O, followed by HCl gas, gives 6-methoxytolyl CH₂Cl ketone, m.p. 44—45°, which with CHMe(CO₂Et)₂ leads to γ -keto- γ -6-methoxy-o-tolyl- α -methyl-n-butyric acid, m.p. 140—141°, reduced (Clemmensen) to γ -6-methoxy-o-tolyl- α -methyl-n-butyric acid, b.p. 139—142°/0.1 mm., the chloride of which gives 1-keto-6-methoxy-2 : 5-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 112—113°. This with MgMeI gives 1-hydroxy-6-methoxy-1 : 2 : 5-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 83—84°, converted by Pd-C at 310° into (I), m.p. 89—90° [1 : 3 : 5-C₆H₃(NO₂)₃ compound, m.p. 146—147°]. The naphthol obtained by dehydrogenation of amyrrin with Zn dust or by hydrogenation and subsequent dehydrogenation by Pd gives 1 : 2 : 5-C₁₀H₅Me₂ [styphnate, m.p. 128—129°; C₆H₂Me(NO₂)₃ compound, m.p. 90—90.5°].

CIX. Glycyrrhetic acid [purified by way of the acetate, m.p. 309—313°, $[\alpha]_D +145^\circ$ in CHCl_3 (1 active H; *Me* ester, m.p. 299—300°)], $\text{C}_{30}\text{H}_{48}\text{O}_8$, dimorphic, m.p. 300—304° and 287—293°, $[\alpha]_D +161^\circ$ (163°) in CHCl_3 , gives a *Me* ester, m.p. 259° (1 active H). None of these compounds gives a colour with $\text{C}(\text{NO}_2)_4$.

R. S. C.

Constitution of resin phenols and their biogenetic relationships. V. Natural phenolic substances of the "dimeric coniferyl type." H. ERDTMAN (Svensk Kem. Tidskr., 1936, 48, 250—257).—A general survey of the more or less completely established structures of compounds of this type indicates that many variants of the diphenylbutane or $1-C_{10}H_7Ph$ scheme occur naturally. The compounds appear to arise by dimerisation of simple components of the safrol, eugenol, and coniferyl alcohol types but the exact course of biogenesis is at present unknown.

H. W.

Lignin and related compounds. XXVIII. Behaviour of lignin towards activated hydrogen. R. G. D. MOORE and H. HIBBERT (Canad. J. Res., 1936, 14, B, 404—407).—The absence of ethylenic linkings in lignin is suggested by observations that fully methylated lignin (from spruce wood-meal; 34—35% OMe) is not reduced catalytically using either Adams or Raney-Ni catalysts in EtOH or AcOH at 55—60°/45 lb. per sq. in. J. W. B.

J. W. B.

[Dioxan lignin and the pigment of ebony wood.] E. WEDEKIND (Ber., 1936, 69, [B], 2521—2522; cf. A., 1936, 207).—A reply to Hilpert *et al.* (A., 1936, 858). H. W.

H. W.

3- and 6-Membered cyclic oxido-compounds. II. W. MADELUNG and M. E. OBERWEGNER (Annalen, 1936, 526, 195—251; cf. A., 1932, 62).—The crude product (I) obtained from desyl chloride and NaOMe contains small amounts of *trans*-($\text{CH} \cdot \text{C}_6\text{H}_4\text{Bz}$)₂ and (*cis*)- α -2 : 5-dimethoxy-2 : 3 : 5 : 6-tetraphenyldioxan (II), m.p. 223°, whereas that (III) derived from desyl bromide contains (II), $\text{CHPhBz} \cdot \text{OH}$, and $\text{CHPhBz} \cdot \text{OMe}$. Distillation of (I) under diminished pressure affords α -methoxy- α - β -diphenyloxan, b.p. 194—196°/16 mm. With minor amounts

of the isomeric dibenzoylstilbenes (IV) whereas (III) yields $\text{OMe}\cdot\text{CHPhBz}$, a little $\text{CHPhBz}\cdot\text{OH}$, and tetraphenyldioxin, but no (IV). (I) and (III) behave similarly when treated with HCl in light petroleum except that (I) gives small amounts of (IV). The same products are formed from (I) or (III) and HCl-MeOH as from $\text{CHPhBz}\cdot\text{OH}$. (II) passes at 250° into $\text{CHPhBz}\cdot\text{OMe}$. An improved prep. of *trans*-2:3:5:6-tetraphenyldioxan (V), m.p. 285° (cf. Irvine *et al.*, J.C.S., 1907, 91, 1391; Bergmann *et al.*, A., 1930, 1438), and *trans*-methoxytetraphenyldioxan (VI), m.p. 185° , from $\text{CHPhBz}\cdot\text{OH}$ and HCl-MeOH is described. (II) in C_6H_6 is transformed by HCl into $\text{CHPhBz}\cdot\text{OH}$ and a little $\text{CHPhBz}\cdot\text{OMe}$ whereas (V) yields (VI) and (VI) is largely unchanged, but gives a little *cis*-stilbenediol dibenzoate and tetraphenyldioxadiene (VII); the latter is readily obtained by treating the crude product of the action of HCl-MeOH on $\text{CHPhBz}\cdot\text{OH}$ with boiling Ac_2O containing ZnCl_2 or FeCl_3 . Treatment of (VII) with dry HCl in C_6H_6 yields *cis*-chlorotetraphenyldioxan, $\text{C}_{23}\text{H}_{21}\text{O}_2\text{Cl}$, converted by MeOH into *cis*-methoxytetraphenyldioxan, m.p. 155° ; under similar conditions (VI) gives a mixture of ethers. With EtOH the *cis*-Et ether, m.p. 163° , is produced, isomerised by HCl-EtOH or boiling AcOH to the *trans*-compound, m.p. 192° . *cis*-(VIII), m.p. 156° , and *trans*-(IX)-*Acetoxytetraphenyldioxan*, m.p. 228° , are described. (VII) with Br in CS_2 affords 2:3-dibromotetraphenyldioxan, m.p. 226° (decomp.) after softening at 220° , converted by boiling MeOH into *trans*-, m.p. 292° , and *cis*-, m.p. 198° , -2:3-dimethoxytetraphenyldioxan; the corresponding *Et* ethers have m.p. 248° and about 295° , respectively. 2:3-*Deacetoxytetraphenyldioxan*, m.p. 297° , is described. (VII) is transformed by conc. H_2SO_4 into the very hygroscopic green oxonium salt, formulated $\left[\begin{smallmatrix} \text{CPh}\cdot\text{O}\cdot\text{CPh} \\ \text{CPh}\cdot\text{O}\cdot\text{CPh} \end{smallmatrix}\right]^+ \text{SO}_4$ since SO_2 is also produced and gives (VII) and (?) H_2O_2 or (?) $\text{H}_2\text{S}_2\text{O}_8$ when treated with H_2O and the corresponding Me ether or acetate when treated with MeOH or NaOAc . When kept with H_2SO_4 the green salt passes into a red compound (corresponding *perchlorate*) in which only 1 O appears to participate in salt formation whereas the composition of the (not isolated) violet oxonium salts is indicated by the formation when (VII) is added to a solution of the green salt. The substance described as 2-acetoxy-2:3:5:6-tetraphenyl- Δ^5 -dioxan, m.p. 174° (*loc. cit.*), is proved to be 2:3-*oxidotetraphenyldioxan*. (VIII) or (IV) is converted by boiling $\text{AcOH-H}_2\text{O}$ into a mixture of *cis*-(X), m.p. 154° , and *trans*-(XI), m.p. 198° (decomp.), -2:3-*oxidotetraphenyldioxan*. (X) is partly converted into (XI) by boiling AcOH , yields *cis*-($\text{CH}\cdot\text{C}_6\text{H}_4\text{Bz}$)₂, m.p. 211° , when treated with AcOH containing HCl or H_2SO_4 , and gives $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{K}$ and CH_2PhBz when boiled with KOH-EtOH . The behaviour of (XI) is in the main similar. Hydrogenation (Pd in EtOAc) of (VII) gives *cis*-tetraphenyldioxan (X), m.p. 165° , which slowly reacts with Br in CS_2 giving benzil and α -stilbene dibromide, m.p. 239° , whereas reduction of (VII) with Na and amyl alcohol in C_6H_6 at $50-60^\circ$ leads to *trans*-tetraphenyldioxan (XI), m.p. $245-247^\circ$, with small amounts of α -tetraphenyldioxan, m.p. 152° , and β -tetraphenyl-

dioxan (XII), m.p. 305°; the tetraphenylethyl ether $C_{28}H_{26}O$, m.p. 131°, is formed as by-product. Complete reduction of (XI) by Na and amyl alcohol gives only the dioxans, whereas that of (X) occurs very slowly, giving mainly unchanged material with a little of the same products. Catalytic hydrogenation of (XI) gives (XII), γ -, m.p. 285°, and δ -, m.p. 143°, -tetraphenyldioxan. $CHPhBz\cdot OH$ in $CHCl_3$ is converted by the successive action of 70% $HClO_4$ and H_2SO_4 into the desyl ether (XIII), $C_{28}H_{26}O_3$, m.p. 129° (dioxime, m.p. 198°), also obtained similarly from (VII); it is converted by cold KOH - $EtOH$ into $BzOH$, benzil, and CH_2PhBz and by the hot reagent into CH_2PhBz , $BzOH$, and $OH\cdot CPh_2\cdot CO_2H$. Similar treatment of (VI) affords (XIII) and the isodesyl ether, m.p. 88° [monoxime, m.p. 152° (decomp.)], which resembles (XIII) in its behaviour towards acid and alkali. The conversion of $CHPhBz\cdot OH$ into isobenzoin and polymeric benzoin is described.

H. W.

Velocity of reaction of furfuraldehyde with acetone, and its application to the determination of furfuraldehyde. E. K. NIKITIN (J. Gen. Chem. Russ., 1936, 6, 1278—1285).—5 ml. of 0.1% aq. $COMe_2$ and 5 ml. of H_2O are shaken with 5 ml. of solution, containing approx. 0.02% of furfuraldehyde (I), 5 ml. of 60% aq. KOH are added, and the mixture is kept at 20° for 12 min. The turbidity developed is compared with that given by a similar mixture containing 5 ml. of 0.005% (I) in place of 5 ml. of H_2O . The concn. of (I) is given by $0.005/[\sqrt{(h_1/h_2)} - 1]$, where h_1 and h_2 are the readings of the first and second solutions, respectively.

R. T.

Syntheses in the pyran group. *cis*-Tetrahydropyran-2 : 6-dicarboxylic acid. W. CZORNO-DOLA (Rocz. Chem., 1936, 16, 459—465).—Pyran-2 : 6-dicarboxylic acid (I) or its Me_2 ester are readily hydrogenated (Pt catalyst) to *cis*-tetrahydropyran-2 : 6-dicarboxylic acid (II) (anhydride, m.p. 71°; chloride, an oil), or its Me_2 ester, m.p. 53—54°. Attempts to convert (II) into the *trans*-modification were unsuccessful. (I) in aq. Na_2CO_3 and $Na-Hg$, in a CO_2 atm., yield its H_2 -derivative, m.p. 210°, which is further hydrogenated to (II) in presence of Pt.

R. T.

Hydroxy-carbonyl compounds. XII. 5 : 7-Dihydroxycoumarin. R. G. HEYES and A. ROBERTSON (J.C.S., 1936, 1831—1832).—2-Hydroxy-4 : 6-dimethoxybenzaldehyde, $NaOH$, and $CN\cdot CH_2\cdot CO_2H$, followed by HCl , give 5 : 7-dimethoxycoumarin-3-carboxylic acid, m.p. 249° (decomp.), which is decarboxylated to 5 : 7-dimethoxycoumarin (citrepten) (cf. Malkin *et al.*, A., 1931, 353). Phloroglucinaldehyde or 2 : 4 : 6-triacetoxybenzylidene diacetate with $NaOAc$ and Ac_2O similarly yields 5 : 7-diacetoxycoumarin.

F. R. S.

Synthesis of rotenone and its derivatives. X. 6 : 7-Dimethoxychroman-4-one. H. F. BIRCH, A. ROBERTSON, and T. S. SUBRAMANIAM (J.C.S., 1936, 1832—1834).— β -3 : 5-Dimethoxyphenoxypropionic acid, m.p. 136—137°, prepared from $CH_2Cl\cdot CH_2\cdot CO_2Na$ and 1 : 3 : 5-OH- $C_6H_3(OMe)_2$, with P_2O_5 gives 6 : 7-dimethoxychroman-4-one, m.p. 123—124°, identical with the product obtained by oxidation of netoric acid

(Takei *et al.*, A., 1932, 400). The chromanone with veratraldehyde forms 6 : 7-dimethoxy-3-veratrylidene-chroman-4-one, m.p. 156.5—157.5° (-furfurylidene-compound, m.p. 138—139°), and with 1 : 2 : 4- $CHO\cdot C_6H_3(OH)\cdot OMe$ yields 7 : 6 : 7'-trimethoxy-chromeno-4' : 3' : 2 : 3-benzopyrylium ferrichloride, m.p. 256—257° (decomp.). β -3 : 5-Dimethoxyphenoxypropionic acid, m.p. 128—129°, prepared from 1 : 3 : 5-OH- $C_6H_3(OMe)_2$ and $CH_2Cl\cdot CH_2\cdot CO_2Na$, is cyclised to 5 : 7-dimethoxychroman-4-one, m.p. 99°. F. R. S.

Usnic acid. IV. Synthesis of 4 : 6-dimethoxy-3 : 5-dimethylcoumarone-2-acetic acid. H. F. BIRCH, D. G. FLYNN, and A. ROBERTSON (J.C.S., 1936, 1834—1837).— α -3-Methoxyphenoxypropionic acid, m.p. 93—94° (amide, m.p. 102°), prepared from $m\text{-}OH\cdot C_6H_4\cdot OMe$ and $CHMeBr\cdot CO_2Et$, is converted into the chloride, which with $AlCl_3$ yields 6-methoxy-2-methyl-3-coumaranone, b.p. 120—125°/1 mm. (2 : 4-dinitrophenylhydrazones, m.p. 206°), and this with Zn and $CH_2Br\cdot CO_2Et$ affords 6-methoxy-2-methylcoumarone-3-acetic acid, m.p. 115—116°. 1 : 3 : 5-OH- $C_6H_3(OMe)_2$ and $CH_2Br\cdot CO_2Et$ yield the *Et* ester, b.p. 188—190°/16 mm., of α -3 : 5-dimethoxyphenoxypropionic acid, m.p. 115—116°, which is converted through the chloride with $AlCl_3$ into 4 : 6-dimethoxy-2-methyl-3-coumaranone, m.p. 74—75° (2 : 4-dinitrophenylhydrazones, m.p. 240°), mixed with some 4 : 6-dimethoxy-3-phenyl-2-methylcoumarone, m.p. 125°. The coumaranone with $CH_2Br\cdot CO_2Et$ and Zn forms the *Et* ester, m.p. 55—57°, of 4 : 6-dimethoxy-2-methylcoumarone-3-acetic acid, m.p. 147—148°. Reduction ($Pd-H_2$) of 4-benzoyloxy-2 : 6-dimethoxybenzaldehyde, m.p. 122—123°, affords C-methylphloroglucinol β - Me_2 ether, m.p. 148—149°, which with $CH_2Br\cdot CO_2Et$ gives α -3 : 5-dimethoxy-4-methylphenoxypropionic acid, m.p. 123—123.5°. The corresponding chloride with $AlCl_3$ yields 4 : 6-dimethoxy-2 : 5-dimethylcoumaranone, m.p. 66—67°, which with Zn and $CH_2Br\cdot CO_2Et$ gives 4 : 6-dimethoxy-2 : 5-dimethylcoumarone-3-acetic acid, m.p. 179—180°. This acid is isomeric and not identical with O-dimethylpyrousnic acid (cf. Asahina *et al.*, A., 1936, 1104).

F. R. S.

Constitution of ayapanin. P. K. BOSE and A. C. ROY (J. Indian Chem. Soc., 1936, 13, 586—587).—Ayapanin, m.p. 114—115° (cf. Nag and Bose, A., 1934, 1421), isolated from the leaves of *Eupatorium ayapana*, is shown to be 7-methoxycoumarin. Two other compounds, m.p. 220—221° (termed *ayapin*) and m.p. 109°, have also been isolated.

H. G. M.

Alpinone, a benzopyrone derivative. Y. KIMURA and M. HOSHII (Proc. Imp. Acad. Tokyo, 1936, 12, 285—288).—Alpinone (3 : 5-dihydroxy-7-methoxy-2-phenyl-2-methyl-2 : 3-dihydrobenzo-1 : 4-pyrone) (I), m.p. 178° [Ac_2 , m.p. 108°, and Bz_2 derivatives, m.p. 208—209°; Me_2 ether (II), m.p. 115°; oxime, m.p. 203—204°; semicarbazone anhydride, m.p. 200—201°], with boiling MeI affords noralpinone, $C_{18}H_{14}O_5$, m.p. 136—137° (Bz_2 derivative, m.p. 203°). (I) with boiling 30—50% KOH (H_2 atm.) affords mainly izalpinin (III), whereas with hot 10—20% KOH (H_2 atm.), apolpinone (3 : 5-dihydroxy-7-methoxy-2-phenyl-2 : 3-dihydrobenzo-1 : 4-pyrone) (IV), m.p. 148° [Me_2 ether (V), m.p. 108—109°], mainly is formed with loss of 1 CH_3 ; some (IV) is converted into (III). (II) with boiling 5%

KOH affords 2-hydroxy-4:6-dimethoxyphenyl α -methoxystyryl ketone, m.p. 112° (also synthesised from 2-hydroxy-4:6-dimethoxy- ω -methoxyacetophenone and PhCHO), converted by boiling EtOH-HCl into the Me₂ ether of (IV) and thence into (V). (I) with 3% H₂O₂ in cold 3% KOH affords some COPhMe, which indicates that 1 Me is in position 2. The skeletons of (I), (IV), and fustin (cf. A., 1935, 757) are similar since their ultra-violet absorption spectra are almost identical. J. L. D.

Colouring matter of red cabbage. II. I. CHEMIELEWSKA (Rocz. Chem., 1936, 16, 384—387).—*Rubrobrassicin chloride* (I), isolated from red cabbage, is a compound of an unidentified biose with methyl-7- or -5-sinapylcyanidin. (I) when warmed with MeOH-Et₂O yields rubrobrassicin chloride, C₂₈H₃₃O₁₆Cl (A., 1934, 336), and *Me sinapate*, m.p. 91—92°. R. T.

Colouring matter of Hibiscus Sabdariffa, L. (hiviscin). II. R. YAMAMOTO and Y. OSIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 258—262; cf. A., 1932, 1296).—Pure hiviscin chloride, C₂₆H₂₀O₁₆Cl₃H₂O, m.p. 178°, with 17% HCl gives glucose, a (?aldo)pentose, and delphinidin chloride, identified by its colour reactions, absorption spectrum, and by conversion into α - γ -2:4:6:3':4':5'-hexamethoxydiphenylpropane. R. S. C.

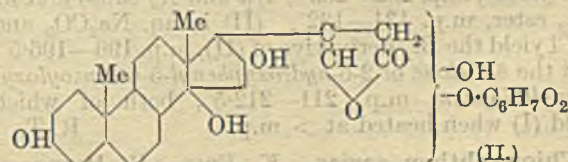
Synthesis of chrysin and other hydroxy-flavones. R. SEKA and G. PROSCHE (Monatsh., 1936, 69, 284—291).—Gradual addition of CPh:C:COCl in PhNO₂ to a well-cooled solution of 1:3:5-C₆H₃(OH)₃ and AlCl₃ in PhNO₂, followed by removal of the solvent with steam and sublimation of the dried, residual resin in a vac. gives 5:7-dihydroxyflavone (chrysin), m.p. 274—275°. Similarly 1:3-C₆H₄(OH)₂ and 1:2:3-C₆H₃(OH)₃ afford 7-hydroxyflavone, m.p. 240.8°, and 7:8-dihydroxyflavone, m.p. 240—241°, respectively. Attempts to condense CPh:C:COCl with 1:2- or 1:3-C₆H₄(OH)₂ were fruitless. 1:3:5-C₆H₃(OH)₃ and 3:4-(OMe)₂C₆H₃:C:C:COCl or 3:4-CH₂O₂:C₆H₃:C:C:COCl appear to give hydroxyflavones. The application of sublimation in a high vac. to the purification of natural and synthetic 3':5:7-trihydroxy-4'-methoxyflavanone (hesperitin) and synthetic 4':5:7-trihydroxy-3'-methoxyflavanone (homoriodictyol) is described. H. W.

Calotropin, the African arrow poison. I. G. HESSE and F. REICHENEDER (Annalen, 1936, 526, 252—276).—Extraction of the dried leaves and stalks of *Calotropis procera* with 50% EtOH at 40—50° and treatment of the extract with Pb(OAc)₂ followed by concn. and extraction with CHCl₃ leaves a solution from which *calotropagenin* (I), m.p. 240°, is removed by charcoal. The CHCl₃ solution is washed with *N*-Na₂CO₃ and treated with light petroleum, thus giving the compound, C₂₉H₄₀O₉.CHCl₃, decomp. 221°, from which by treatment with boiling C₆H₆ followed by crystallisation from EtOH or EtOAc and desiccation at 120°/high vac. calotropin (II), C₂₉H₄₀O₉ (? C₂₉H₄₂O₉), m.p. 221° (decomp.) when rapidly heated, [α]_D +55.7° in MeOH (monohydrate), is obtained. (II) is very hygroscopic, stable to air, and gives a positive Legal test. The amorphous Me ether has m.p. about 165°. Fission of (II)

with *N*-NaOH under N₂ gives *ψ -calotropaic acid* (III), C₂₃H₃₄O₇, decomp. 228° after marked softening at 190—195° (Et ester, m.p. 224°), *ψ -calotropagenin* (IV), C₂₃H₃₂O₆, m.p. 241° (decomp.), and a very strongly reducing substance (V). Similar treatment with Ba(OH)₂-MeOH gives an insol. Ba salt which, when dry, ignites spontaneously on exposure to air; (V) is not present in the mother-liquors. (II) in MeOH containing Ba(OH)₂ readily absorbs atm. O₂, whereby > one change appears to occur. The solution contains a substance, C₂₉H₄₂O₁₀, m.p. 154° which loses CO₂ at 100° giving the compound, C₂₈H₄₂O₈, m.p. 224°, whilst (V) is also present. When (II) is heated at 230°/high vac. it gives (V) as a cryst. sublimate whilst (I) is obtained by chromatographic analysis of the residue. Both fissions proceed similarly with regard to (V) but differently with respect to the other products owing to the action of alkali on (I) whereby (III) and (IV) are produced. To eliminate this effect (II) is heated with conc. Na₂B₄O₇ in absence of air, whereby (V) and the lactone *isocalotropagenin*, m.p. 251° (converted by cautious treatment with alkali into *isocalotropaic acid*, C₂₃H₃₄O₇, decomp. 156°), are produced, also formed from (I). (V), m.p. 84° [dinitrophenyllosazone (VI), decomp. 230°], is methylreductic acid, $\begin{matrix} \text{OH}\cdot\text{C}-\text{CO} \\ \text{OH}\cdot\text{C}-\text{CH}_2 \end{matrix} > \text{CHMe}$ (VI) or

$\begin{matrix} \text{OH}\cdot\text{C}-\text{CO} \\ \text{OH}\cdot\text{C}-\text{CHMe} \end{matrix} > \text{CH}_2$. It reduces Tollens' reagent, neutral AgNO₃, acid I, cold Fehling's solution, and methylene-blue. KMnO₄, CrO₃, or H₂O₂-EtO₂ do not transform it into cryst. products. HNO₃ gives H₂C₂O₄ in good yield. Under defined conditions Ag₂O transforms (V) into methylsuccinic acid, the change following the course

(VII) $\rightarrow \begin{matrix} \text{CO}-\text{CO} \\ \text{CO}\cdot\text{CH}_2 \end{matrix} > \text{CHMe}$ [from which (VI) is derived] $\rightarrow \text{CHO}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ or $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CHO}$ (which gives a *phenylhydrazidediphenylhydrazone*, C₂₄H₂₆ON₆, decomp. 148°) $\rightarrow \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ (the *dinitrophenylhydrazone*, decomp. 188°, differs from that of α -keto- α' -methylglutaric acid) $\rightarrow \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. Attempts to prepare (V) from rhamnose were unsuccessful; at 200°/0.5 mm. a reducing distillate is obtained which gives minimal amounts of a red compound with (NO₂)₂C₆H₃:NH·NH₂ but acidic hydrolysis does not afford reducing substances, which are produced in minor amount by alkaline treatment but not by Na₂B₄O₇. (I) is a new aglucon of the cardiac poisons class and is very closely related to strophanthidin. Of the 6 O 2 are present in the enol-lactone ring and 2 are in OH groups in the neighbourhood of the side-chain which give rise to two series of transformation products. The function of the remaining 2 O is not established but by analogy the presence of OH at C₃ may be assumed. Thermal decomp. of (II)



gives (I) and (V) in at least 70% yield and no other volatile material is formed. In harmony the formula

of (II) is obtained by summation of (I) and (V). Towards boiling 1% H_2SO_4 (II) is stable and under more drastic conditions it gives *anhydrocalotropin*, m.p. 207°, which gives (V) when heated in vac. It therefore appears certain that (V) exists pre-formed in (II) and the annexed structure for (II) is suggested.

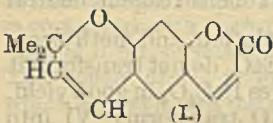
H. W.

Compound of dioxan with perchloric acid. C. SMEETS (*Natuurwetensch. Tijds.*, 1937, 19, 12—15).—Dioxan forms a *perchlorate*, $\text{C}_4\text{H}_8\text{O}_2 \cdot \text{HClO}_4 \cdot \text{H}_2\text{O}$, m.p. 80—82°, and double compounds, $\text{M}(\text{ClO}_4)_2 \cdot 12\text{C}_4\text{H}_8\text{O}_2 \cdot 6\text{H}_2\text{O}$, in which $\text{M} = \text{Ni}, \text{Cu}, \text{Co}$, and Mn . Dioxan can be determined by oxidation with excess of $\text{K}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 .

S. C.

Constituents of the bark of *Zanthoxylum americanum* (Mill). II. Xanthyletin. (Miss) J. C. BELL and A. ROBERTSON (*J.C.S.*, 1936, 1828—1831).—From the mother-liquors left after removing xanthoxyletin, *xanthyletin* (I), $\text{C}_{14}\text{H}_{12}\text{O}_3$, m.p. 128—128.5°, has been isolated; (I) is reduced ($\text{Pd}-\text{H}_2$) to the H_2 -derivative, m.p. 124—125°, which with Me_2SO_4 - NaOH yields *o-methyldihydroxanthoxyletinic acid*, m.p. 141—142°, reduced to the *tetrahydro-acid*, m.p. 99—100°, also obtained from *o-methylxanthyletinic acid*, m.p. 193—194° (decomp.), prepared from (I) and Me_2SO_4 . NaOH converts (I) into COMe_2 and resorcinol (*di-p-nitrobenzoate*, m.p. 184—185°).

Ozonolysis of (I) affords 7-hydroxy-6-formylcoumarin, m.p. 253° (decomp.) [*phenylhydrazone*, m.p. 255—257° (decomp.)], which is reduced ($\text{Pd}-\text{H}_2$) to 7-hydroxy-6-methylcoumarin, m.p. 248° (acetate, m.p. 145—146°), also obtained from 1:5:2:4- $\text{CHO} \cdot \text{C}_6\text{H}_4\text{Me}(\text{OH})_2$, NaOAc , and Ac_2O .



Preparation of β -thiophenic [thiophen-3-carboxylic] acid. I. J. RINKES (*Rec. trav. chim.*, 1936, 55, 991—992).—Tetraiodothiophen, m.p. 199—200°, with $\text{Al}-\text{Hg}$ gives 64% of 3-iodothiophen, b.p. 77—80°/11 mm., which with KCN and CuCN in aq. EtOH at 180° affords 62% of thiophen-3-carboxylic acid, m.p. 137—138°.

R. S. C.

New thiophen derivative. J. SAWLEWICZ (*Rocz. Chem.*, 1936, 16, 470—478).—The product obtained by fusing coumarin with S (A., 1936, 997) is shown to be the $\delta\delta$ -dilactone (I), m.p. 331—331.5°, of 2:5-di-*o*-hydroxyphenylthiophen-3:4-dicarboxylic acid (II) (*dichloride*, decomp. 155°; Me_2 ester, m.p. 155.5—156°; *diamilide*, m.p. 264—264.5°). (I) is hydrolysed to (II) by aq. NaOH , and (II) readily regenerates (I) when heated at below the m.p. A solution of (II) in aq. NaOH and Me_2SO_4 afford a mixture of 2:5-di-*o*-anisylthiophen-3:4-dicarboxylic acid (*anhydride*, m.p. 232—233°; Na and Ag salts) and its Me_2 ester, m.p. 131—132°. (II) in aq. Na_2CO_3 and BzCl yield the Bz_2 derivative of (II), m.p. 196—196.5°, and the δ -lactone of 2-*o*-hydroxyphenyl-5-*o*-benzoyloxyphenylthiophen, m.p. 211—212.5°, both of which yield (I) when heated at $>$ m.p.

R. T.

Thionaphthen series. K. FRIES, H. HEERING, E. HEMMECKE, and G. SIEBERT (*Annalen*, 1936, 527, 83—114).—The character of thionaphthen is de-

finitely not benzenoid. In most of its reactions it appears naphthoid and when this is not so the changes appear to require further explanation.

Gradual addition of 33% KOH to $\text{COPh} \cdot \text{CH}_2\text{Br}$ and $\text{m-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SH}$ in EtOH affords *phenacyl m-hydroxyphenyl sulphide*, m.p. 78.5° (*oxime*, m.p. 92°; *Me ether*, m.p. 47°), converted by conc. H_2SO_4 into 5-hydroxy-2-phenylthionaphthen (I), m.p. 81° [*Me ether* (II), m.p. 59°]. (I) is readily converted by Br (1 mol.) in CHCl_3 into 6-bromo-5-hydroxy-2-phenylthionaphthen, m.p. 102° [the *Me ether*, m.p. 113°, is obtained by use of Me_2SO_4 but not by direct bromination of (II)]. Further bromination readily leads to 1:6-dibromo-5-hydroxy-2-phenylthionaphthen, m.p. 128° [*Me ether*, m.p. 177°, obtained by bromination of (II), which then slowly gives 1:4:6-tribromo-5-methoxy-2-phenylthionaphthen, m.p. 164°]. Chlorination of (I) in CHCl_3 gives 1:6-dichloro-5-hydroxy-2-phenylthionaphthen, m.p. 99° (which is not a keto-chloride since it is sol. in alkali, unchanged by SnCl_2 , and does not liberate I from KI), and then 1:4:6-trichloro-5-hydroxy-2-phenylthionaphthen (III), m.p. 113°. Treatment of (I) with a large excess of Cl_2 in CHCl_3 gives 1:3:4:4:6:6-hexachloro-5-keto-2-phenyl-3:4:5:6-tetrahydrothionaphthen, m.p. 167° (decomp.), which liberates I from KI and reacts with SnCl_2 ; it is reduced (Pd -sponge in anhyd. CHCl_3) to (III) or by SnCl_2 in excess of AcOH to 1:4-dichloro-5:6-dihydroxy-2-phenylthionaphthen, m.p. 160° (*diacetate*, m.p. 152°), oxidised by HNO_3 (*d* 1.4) in warm AcOH to 1:4-dichloro-2-phenylthionaphthen-5:6-quinone, m.p. 186°.

4:4'-Dinitro-2:2'-dialdehyddiphenyl disulphide is transformed by treatment with $\text{Na}_2\text{S}-\text{Na}_2\text{CO}_3$ in boiling $\text{EtOH}-\text{H}_2\text{O}$ followed by $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{Na}$ into 4-nitro-2-aldehydophenylthiolacetic acid, m.p. 178°, transformed by boiling 2*N*- NaOH into 4-nitrothionaphthen-1-carboxylic acid (IV), m.p. 237° (*Et ester*, m.p. 166°, also obtained from 4:2-(NO_2)(CHO) $\text{C}_6\text{H}_3 \cdot \text{SBr}$ and $\text{CHAcNa} \cdot \text{CO}_2\text{Et}$; corresponding *chloride*, m.p. 160°), obtained more readily by the successive treatment of 5:2- $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{Cl} \cdot \text{CHO}$ in boiling EtOH with $\text{Na}_2\text{S}-\text{S}$, $\text{NaOH}-\text{Na}_2\text{S}$, and $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{Na}$. (IV) is reduced by FeSO_4 and NH_3 to 4-aminothionaphthen-1-carboxylic acid (V), m.p. 278° (decomp.), chlorinated in AcOH containing conc. HCl to 3:3:5:5:6-pentachloro-4-keto-3:4:5:6-tetrahydrothionaphthen-1-carboxylic acid, m.p. 172° (decomp.). This when heated at 170—180° or rapidly heated to boiling with AcOH containing NaOAc gives

3:3:5:6-tetrachloro-4-keto-3:4-dihydrothionaphthen-1-carboxylic acid, m.p. 213° (decomp.), and when reduced by SnCl_2 in AcOH containing NaOAc gives 3:5:6-trichloro-4-hydroxythionaphthen-1-carboxylic acid, m.p. 290°, oxidised by HNO_3 in AcOH to 5:6-dichlorothionaphthen-3:4-quinone-1-carboxylic acid, m.p. 225° (decomp.), also obtained by hydrolysis of the keto-chloride; it is converted by NH_2Ph in EtOH into 5-chloro-6-anilo-4-hydroxy-3-keto-3:6-dihydrothionaphthen-1-carboxylic acid, m.p. 255°. (V) is transformed through the *diazonium* compound into 4-hydroxythionaphthen-1-carboxylic acid, m.p. 264°. When heated with PbO at 280—290° (V) affords 4-aminothionaphthen (VI), m.p. 72° (*Ac derivative*, m.p. 106°), converted by Br in AcOH into

3-bromo-4-aminothionaphthen, m.p. 75° (Ac derivative, m.p. 143°), and by PhCHO into benzylidene-thionaphthyl-4-amine, m.p. 98°. The latter and 4-aminothionaphthen hydrochloride at 180° and then at 200–205° give di-2':3':2'':3'-thiopheno-5-phenyl-5:10-dihydro-1:2:3:8:9-acridine, m.p. 269°. (VI) is transformed by Skraup's reaction into 2':3'-thiopheno-5:6-quinoline, m.p. 88°. 8-Bromo-2':3'-thiopheno-5:6-quinoline, m.p. 132°, is obtained similarly. (VI) couples with PhN₂Cl to 3-benzeneazothionaphthyl-4-amine, m.p. 103° (Ac derivative, m.p. 154°). Exhaustive chlorination of (VI) in AcOH containing HCl leads to 1:2:3:5:6-pentachloro-4-hydroxythionaphthen, m.p. 164°, oxidised by HNO₃ (d 1.4) in AcOH to 1:2:5:6-tetrachlorothionaphthen-3:4-quinone, m.p. 166°, whence 1:2:5-trichloro-4-hydroxy-3-keto-6-anilo-3:6-dihydrothionaphthen, m.p. 270°.

4-Hydroxythionaphthen, m.p. 103° (Me ether, m.p. 44°), obtained by diazotisation of (VI), is brominated in AcOH containing NaOAc to 3-bromo-4-hydroxythionaphthen, m.p. 112° [whence 3-bromo-2-nitro-4-hydroxythionaphthen, m.p. 173° (decomp.)], or 2:3-dibromo-4-hydroxythionaphthen, m.p. 103°. The latter is oxidised by HNO₃ (d 1.42) in CHCl₃ to 2-bromothionaphthen-3:4-quinone, sublimation, softening, and decomp. 130°, reduced by SO₂ to 2-bromo-3:4-dihydroxythionaphthen, m.p. 248° (also +C₆H₆) (diacetate, m.p. 140°). 2-Bromo-4-hydroxy-3-keto-6-anilo-3:6-dihydrothionaphthen, decomp. 213°, is described.

2-Nitrothionaphthen in H₂SO₄ is transformed by KNO₃ at >4° into 2:3:6-trinitrothionaphthen, m.p. 196°, or if less KNO₃ is used into 2:3-dinitrothionaphthen (VII), m.p. 199.5°, accompanied by dinitrothionaphthen B (labile α-form, m.p. 98–99°, and β-variety, m.p. 119–121°) and dinitrothionaphthen C, m.p. 171°, of unexplained constitution. Reduction of (VII) in EtOH by SnCl₂-HCl gives the very sensitive 2:3-diaminothionaphthen [stannichloride (VIII); Ac₂ derivative, m.p. 167°]; treatment of (VIII) with boiling 20% HCl followed by NaOH and K₃Fe(CN)₆ leads to (?) 4:4'-diaminothioindogotin in very small yield. (VII) is transformed by boiling EtOH-NH₃-H₂O followed by H₂S into 3-nitrothionaphthen, m.p. 88°, whence 3-aminothionaphthen, m.p. 59° (Ac derivative, m.p. 134°), which couples with SO₃H·C₆H₄·N₂Cl to the salt, C₁₄H₁₀O₃N₃S₂Na, reduced by Na₂S₂O₄ to 3:6-diaminothionaphthen, m.p. 114° (decomp.) [dihydrochloride, m.p. 151° (decomp.)]; Ac₂ derivative, m.p. 287°, which does not react with benzil.

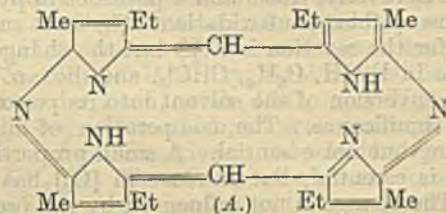
The following compounds are incidentally described: di-p-hydroxyphenacyl disulphide, m.p. 215°, which could not be converted into 2:5-dihydroxythionaphthen; di-p-hydroxyphenacyl sulphide, m.p. 190°; m-methoxyphenylthioacetic acid, m.p. 64°, from which 2-hydroxy-5-methoxythionaphthen could not be obtained.

H. W.

Curtius degradation in the pyrrole series. III. Autoxidation in the pyrrole series and a new synthesis of di-imidoporphyrins. W. METZGER and H. FISCHER (Annalen, 1936, 527, 1–37; cf. A., 1934, 1227).—4-Methyl-2-dichloromethyl-3-ethylpyrrole-5-carboxylazide (I) (improved prep.) is transformed by cold MeOH into 2-aldehydo-4-methyl-3-

ethylpyrrole-5-carboxylazide, m.p. 67–68° (decomp.), which is unsuited for the methene condensation. It is transformed by boiling CH₂Ph·OH-xylene into 2-aldehydo-4-methyl-3-ethylpyrrole-5-benzylurethane, m.p. 209° (decomp.) (corresponding aldazine, C₃₂H₃₆O₄N₆, m.p. 220°). 3-Bromo-4-methyl-2-dichloromethylpyrrole-5-carboxylazide is similarly transformed into 3-bromo-2-aldehydo-4-methylpyrrole-5-benzylurethane (II), m.p. 187° (decomp.) [aldazine, m.p. 254° (decomp.)], accompanied by the methene in considerable amount. (II) is transformed by 2:4-dimethylpyrrole (1 mol.) in HBr-AcOH into the two symmetrical pyrromethenes, $\begin{array}{c} \text{CH}-\text{CMe} \\ \text{CMe}_2\cdot\text{NH} \end{array} > \text{C}=\text{CH} < \begin{array}{c} \text{CMe} \\ \text{N}(\text{HBr})\cdot\text{CMe} \end{array}$

m.p. 251°, and $\begin{array}{c} \text{CH}_2\text{Ph} \quad \text{CMe}\cdot\text{CBr} \\ \text{CO}_2\text{NH}\cdot\text{C}-\text{NH} \end{array} > \text{C}=\text{CH} < \begin{array}{c} \text{CBr}\cdot\text{CMe} \\ \text{N}-\dot{\text{C}}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph} \end{array}$, m.p. 195° (decomp.), whereas with 2 mols. it gives 3-bromo-4:3':5'-trimethylpyrromethene-5-benzylurethane, decomp. 158° (picrate, decomp. 165°). (I) is transformed by boiling EtOH (the liberated HCl acts as condensing agent) into 4:4'-dimethyl-3:3'-diethylpyrromethene-5:5'-diethylurethane, m.p. 147° [mono-, m.p. 179° (decomp.)], and di-hydrochloride; Bz₂ derivative, m.p. 125° (decomp.); Ac₂ compound, decomp. 174°, and its picrate, m.p. 181° (decomp.)]. 4:4'-Dimethyl-3:3'-diethylpyrromethene-5:5'-diethylurethane (III) readily undergoes oxidative autocondensation in alkaline or acid



medium to the βδ-di-imidoætioporphyrin II (A), m.p. >300°, also obtained when (III) is heated with (COCl)₂ in Et₂O or with conc. HCl at 110° and, best, by treatment of it with NHPh·NH₂ at 160–200°. 5-Carboxy-2:4-dimethylpyrrole-3-propionic acid is transformed by N₂H₄·H₂O at 130° into 2:4-dimethylpyrrole-5-carboxylhydrazide-3-propionhydrazide, m.p. 248° (decomp.) [dihydrochloride, decomp. 258°; p-dimethylaminobenzylidene derivative, C₂₈H₃₅O₂N₇, m.p. 242° (decomp.)]. Et 2:3:5-trimethylpyrrole-4-carboxylate is converted with difficulty into 2:3:5-trimethylpyrrole-4-carboxylhydrazide, m.p. 196° [CHPh derivative, m.p. 230°; condensation product, C₁₆H₁₆O₂N₄, m.p. 283° (decomp.), with isatin], whence 2:3:5-trimethylpyrrole-4-carboxylazide, m.p. 108° (decomp.). 2:4-Dimethyl-3-ethylpyrrole-5-carboxylazide is transformed by boiling CH₂Ph·OH-xylene into the compound, C₁₆H₂₀O₃N₂, m.p. 121° (instead of the expected urethane), hydrogenated (Pd-sponge-MeOH-AcOH) to the substance, C₁₈H₁₄O₂N₂, m.p. 180° (decomp.). 1-Amino-2:4-dimethyl-3-ethylpyrrole (?), m.p. 208°, is incidentally described. Autoxidation of pyrroles is conveniently studied by exposing the base in a suitable solvent in open or loosely-closed Erlenmeyer flasks to diffused daylight for several days. Thus 2:4-dimethyl-3-ethylpyrrole

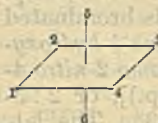
affords the peroxide $\left(\begin{smallmatrix} \text{CEt}\cdot\text{CMe} \\ \text{CMe}\cdot\text{NH} \end{smallmatrix} \right)_2 \cdot \text{C}\cdot\text{O}$, m.p. 219—220°, also obtained as by-product of its oxidation by H_2O_2 in $\text{C}_5\text{H}_5\text{N}$ or from cryptopyrrole ether and transformed by Br in AcOH into 4-methyl-2-bromo-methyl-3-ethylpyrrolen-5-one, $\begin{smallmatrix} \text{CEt}\cdot\text{C}(\text{CH}_2\text{Br}) \\ \text{CMe}\cdot\text{CO} \end{smallmatrix} \gg \text{N}$, m.p. 140—141°. Di-(2:3-dimethyl-4-ethylpyrrol) 5-peroxide, m.p. 228° (decomp.), and di-(2:3:4-trimethylpyrrol) 5-peroxide, m.p. 245°, are formed similarly. Cryptopyrroles with CO_2Et at 1 or 5 remain unchanged. Experiments with pyrrolepropionic acids were unsuccessful but Me 2:4-dimethylpyrrole-3-propionate readily yields the corresponding peroxide, m.p. 202° (decomp.), brominated at 100° to a substance, m.p. 172° (decomp.). Autoxidation of Me 2:3-dimethylpyrrole-4-propionate appears to yield Me 5:5-dihydroxy-2:3-dimethylpyrrolene-4-propionate, $\begin{smallmatrix} \text{CMe}\cdot\text{CMe} \\ \text{N}\cdot\text{C}(\text{OH})_2 \end{smallmatrix} \gg \text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, m.p. 137° (decomp.), brominated mainly to Me 3-methyl-2-dibromomethylpyrrolen-5-one-4-propionate, m.p. 142° (decomp.). 2:4-Dimethylpyrrole (IV) in Et_2O is slowly autoxidised to 2:4-dimethylpyrrolen-5-one hydrate, m.p. 145°, decomp. 205°, converted by boiling Ac_2O containing KOAc into the substance, $\text{C}_{12}\text{H}_{18}\text{ON}_2$, m.p. 160°. Di-(3-methyl-4-ethylpyrrol) 2-peroxide, m.p. 281° (decomp.), and di-(Me 3-methylpyrrol-4-propionate) 2-peroxide, m.p. 193° (decomp.), are described. Generally, free 3 and 4 positions in pyrroles are not susceptible to autoxidation. The most suitable medium for the reaction is Et_2O but the change proceeds also in EtOH, C_6H_6 , CHCl_3 , and dioxan. The possible conversion of the solvent into its peroxide is without significance. The co-operation of light is stimulating but not essential. A small proportion of moisture is essential, but increase in $[\text{O}_2]$ has little effect. The change is not influenced by the presence of HCN or carbimides but is nullified by Ac_2O . The peroxides do not liberate I from HI or decolorise indigotin in conc. H_2SO_4 and therefore do not contain active O. Ring fission occurs with boiling dil. NaOH. Oxidation of certain non-autoxidisable pyrroles with H_2O_2 is best effected in EtOH- Et_2O . Thus Et 2:4-dimethylpyrrole-3-carboxylate is converted into Et 5-hydroxy-2:4-dimethylpyrrole-3-carboxylate, m.p. 127°, and 5-hydroxy-2:4-dimethylpyrrole-3-carboxylic acid, m.p. 196° (decomp.), is obtained similarly; both are unstable to alkali. In hot EtOH (IV) is converted by H_2O_2 into 3:5-dihydroxy-2:4-dimethylpyrrole, m.p. 175°, whereas in cold solution the product, m.p. 130—131° (decomp.), is probably $\begin{smallmatrix} \text{C}(\text{OH})\cdot\text{CMe} \\ \text{CMe}\cdot\text{C}(\text{OH})_2 \end{smallmatrix} \gg \text{N}$, transformed by Br-AcOH at 100° into the compound, $\text{C}_6\text{H}_5\text{O}_3\text{NBr}_2$, decomp. 126°. 2- and 3-Methylpyrrole yield compounds, $\text{C}_5\text{H}_9\text{O}_3\text{N}$, m.p. 154° (decomp.), and $\text{C}_6\text{H}_{11}\text{O}_3\text{N}$, m.p. 143° (decomp.), respectively. The hydroxypyrroles do not give a coloration with FeCl_3 in EtOH. There appears to be no relationship between capability of autoxidation and behaviour towards H_2O_2 . Substituents which impede the former are without action on the latter process. Autoxidisability of aminopyrroles and their carbamates exhibits the same regularities as that of other pyrroles. The process is linked with the basic nature of the

pyrrole mol. and substituents which enhance this character increase the tendency towards autoxidation.

H. W.

Absorption spectra of dihydropyridine compounds.—See A., III, 68.

Pyridine complexes of quadrivalent platinum derivatives. A. M. RUBINSCHTEIN (Ann. Sect. Platine, 1936, 13, 21—57).—Cleve's salt and $\text{C}_5\text{H}_5\text{N}$ at 100° give a ppt. of $\text{Pt}(\text{C}_5\text{H}_5\text{NCl})_2\text{Cl}_2$, whilst the product with Gérard's salt is $[\text{PtNH}_3\text{C}_5\text{H}_5\text{NNH}_3\text{ClC}_5\text{H}_5\text{NCl}]\text{Cl}_2\cdot 4\text{H}_2\text{O}$ (I) (the substituents are given in the order shown in the figure). $[\text{PtC}_5\text{H}_5\text{NNH}_3\text{C}_5\text{H}_5\text{NNH}_3\text{Cl}_2]\text{Cl}_2\cdot 4\text{H}_2\text{O}$ (oxalate; platini- and platino-chloride) is obtained by heating aq. $\text{C}_5\text{H}_5\text{N}$ with Reise's second salt, and treating with Cl_2 the $\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2$ so formed. $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_2(\text{NH}_3)_2\text{Cl}_2]\text{Cl}_2$ is prepared analogously from Peyronne's salt. Pt enCl_4 and $\text{C}_5\text{H}_5\text{N}$ yield $[\text{Pt enCl}_4](\text{C}_5\text{H}_5\text{N})_2$ at room temp., whilst at the b.p. the product is a mixture of $[\text{Pt enC}_5\text{H}_5\text{NCl}_2]\text{Cl}$ and $[\text{Pt enCl}_2\text{C}_5\text{H}_5\text{NCl}]\text{Cl}$; these results contradict those of Schleicher *et al.* (A., 1923, i, 1120). $[\text{Pt en}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2]\text{Cl}_2$ is obtained by chlorinating the product



of reaction of Pt enCl_2 with aq. $\text{C}_5\text{H}_5\text{N}$. Pt enCl_4 and $(\text{NH}_2\cdot\text{CH}_2)_2$ in presence of $\text{C}_5\text{H}_5\text{N}$ affords $\text{Pt en}_2\text{Cl}_4$. Blomstrand's salt (I) and $\text{C}_5\text{H}_5\text{N}$ at 100° afford $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_5\text{H}_5\text{NCl}]\text{Cl}$ (oxalate). (I) and Reise's first salt, in aq. or $\text{C}_5\text{H}_5\text{N}$ solution, give $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2\text{Cl}_2][\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$. The above reactions are in accord with Tscherniaev's law of trans-substitution.

R. T.

Oxidation of cis- and trans-bivalent platinum non-electrolytes by nitric acid.—See A., I, 96.

Pyridine. XXIII. Derivatives of 3-aminopyridine. O. VON SCHÖCKH, A. BINZ, and A. SCHULZ (Ber., 1936, 69, [B], 2593—2605).—2- NH_2 in $\text{C}_5\text{H}_5\text{N}$ directs the first new substituent mainly towards position 5 and to some extent towards 3; further substitution leads to 2- NH_2 -3:5-derivatives. 3- NH_2 directs towards the 2 and 2:6 positions. Gradual addition of 15% H_2O_2 to 3- $\text{C}_5\text{H}_4\text{N}\cdot\text{NH}_2$ (I) in conc. HCl at 70—80° affords mainly 2-chloro-3-aminopyridine (II), b.p. 134—135°/15 mm., m.p. 79—80°, also obtained by reduction of 2-chloro-3-nitropyridine with Fe powder and AcOH. Similar chlorination of (I) at 110° affords also 2:6-dichloro- (III), b.p. 110°/0.2 mm., m.p. 119°, and 2:4:5:6-tetrachloro-, m.p. 143°, -3-aminopyridine. Passage of Cl_2 into a solution of (I) in boiling HCl gives small amounts of (II) and (III); the latter is also obtained by treating (II) or 6-chloro-3-aminopyridine with nascent Cl. (II) with cold Ac_2O gives 2-chloro-3-acetamidopyridine, m.p. 90—91°, whilst with boiling Et_2O 2-chloro-3-diacetamidopyridine, m.p. 67—68°, is ultimately obtained exclusively. 3-Diacetamidopyridine, m.p. 88°, is somewhat less readily prepared. (II), PhCHO , and anhyd. NaOAc at 80—100° yield 2-chloro-3-benzylideneaminopyridine, b.p. 162°/0.6 mm. 2-Chloro-3-hydroxypyridine, m.p. 163°, is obtained from (II) by the diazo-method or from 3- $\text{C}_5\text{H}_4\text{N}\cdot\text{OH}$ and H_2O_2 in boiling concn. HCl. 2-Chloro-3-cyanopyridine has m.p. 107—108°. (II), NaOMe or NaOH, and Cu powder in MeOH at 150° give 3-amino-2-

methoxypyridine, b.p. 116—118°/3 mm., m.p. 68° (*Ac* derivative, m.p. 163°), whence by the diazo-reaction, 3-hydroxy-2-methoxypyridine (IV), b.p. 82°/11 mm., m.p. 68—69°, also obtained from 2-halogeno-3-hydroxypyridines. (IV) and boiling 40% HBr or conc. HI yield 2:3-dihydroxypyridine, m.p. 246°, oxidised to pyridine-2:3-quinone. (I) is converted by 25% NH₃ containing CuSO₄ at 130° into 2:3-diaminopyridine, m.p. 112°; analogous reactions lead to 3-amino-2-methylamino-, m.p. 100—101°, and 2-anilino-, m.p. 141°, pyridine. Gradual addition of H₂O—I-KI to 3-C₅H₄N·OH and Na₂CO₃ in H₂O at room temp. affords 2-iodo-, m.p. 192°, whereas at the b.p. di-iodo-, m.p. 198°, and tri-iodo-, m.p. 156—157°, 3-hydroxypyridine are formed. 2:3-Dihydroxypyridine monoacetate has m.p. 155°. 4-C₅H₄N·OH is converted by NaOH at 290—310° into 2:4-dihydroxypyridine, m.p. 260°. 3-C₅H₄N·NO₂, m.p. 35—36°, is obtained by gradual addition of a suspension of (I) in conc. H₂SO₄ to a mixture of HNO₃ (*d* 1.93) and 30% H₂O₂ at room temp., less advantageously from (I) through the diazo-reaction; it is transformed by Cl₂ at 130—150° into pentachloropyridine, m.p. 124—125°. (I) with ICl in conc. HCl affords 3-aminopyridine iodochloride hydrochloride, m.p. 149°. Addition of H₂O₂ to (I) in aq. HI followed by treatment of the periodide with NaOH causes essentially oxidation with production of 3:3'-azopyridine, m.p. 138°. (I) with nascent Br at 80° or at room temp. appears to give exclusively 2:6-dibromo-3-aminopyridine, m.p. 145°. H. W.

3-Hydroxypyridine. I. Amination and sulphonation. E. PŁĄZEK (Rocz. Chem., 1936, 16, 403—405).—3-Hydroxypyridine (I) and NaNH₂ in *p*-cymene at 130° yield 2:6-diaminopyridine. (I) and H₂SO₄ in presence of (VO)₂(SO₄)₃ at the b.p. afford 3-hydroxypyridine-2(6)-sulphonic acid, identical with that obtained from 3-diazopyridine-2(6)-sulphonic acid. R. T.

N-Hydroxyalkyl-2-pyridones. J. A. GAUTIER (Compt. rend., 1936, 203, 794—796; cf. A., 1933, 720; 1934, 663).—EtOH, PrⁿOH, BuⁿOH, and CH₂Prⁿ·CH₂·OH with epichlorohydrin and H₂SO₄ afford Et, Prⁿ, b.p. 89°/13 mm., Buⁿ, and isoamyl γ -chloro- β -hydroxypropyl ether, respectively, which with hot C₅H₅N afford the hydrochlorides (very hygroscopic) of *N*-substituted pyridines, converted by K₃Fe(CN)₆ into 2-pyridones which are unstable in air and give red colours with FeCl₃. The following are prepared: *N*- γ -ethoxy-, b.p. 186°/14 mm. (*phenylcarbamate*, m.p. 117°), -propoxy-, b.p. 200°/17 mm. (*phenylcarbamate*, m.p. 115°), -butoxy-, b.p. 195—197°/12 mm. (*phenylcarbamate*, m.p. 98°), and -isoamyl- β -hydroxypropyl-2-pyridone, b.p. 211—213°/12 mm. (*phenylcarbamate*, m.p. 126°). J. L. D.

s-Di-2-methyl-6-pyridylthiocarbamide. K. FEIST (Arch. Pharm., 1936, 274, 547—548).—The identity of this substance, m.p. 209° (cf. Töptschew, A., 1936, 612; Feist *et al.*, *ibid.*, 1519), is confirmed. R. S. C.

Preparation of aminoisatin and derivatives [therefrom]. M. HARTMANN and L. PANIZZON (Helv. Chim. Acta, 1936, 19, 1327—1332).—5-Acetamido-oxindole (modified prep.; NO₂-derivative,

m.p. 261°) with CrO₃ in aq. AcOH at 90—110° gives 5-acetamidoisatin, m.p. 286°, and +2H₂O, hydrolysed to 5-aminoisatin, m.p. >360° {sulphate; 5-*N*-Me₂-derivative (prep. by CH₂O in H₂O, not HCO₂H), m.p. 215° [methiodide, m.p. 247—249° (decomp.); methochloride, m.p. 250° (decomp.)]}, which with HNO₂ gives 5-hydroxyisatin, m.p. >360°. R. S. C.

Destructive hydrogenation of quinoline. I. B. RAPOPORT (J. Appl. Chem. Russ., 1936, 9, 1456—1464).—Quinoline and H₂ (MoS₃ catalyst) at 220°/100—110 atm. yield tetrahydroquinoline, whilst at 420—450°/80 atm. the products are C₆H₆, PhMe, PhEt, xylene, naphthenes, CH₄, NH₃, NH₂Ph, NHPH₂, tetrahydroaniline, and dihydroethylaniline. R. T.

By-products of Skraup's quinoline synthesis. E. SUCHARDA and T. MAZONSKI (Ber., 1936, 69, [B], 2719—2721).—*p*-NH₂·C₆H₄·OH, 6- and 8-hydroxyquinoline are obtained as by-products of Skraup's synthesis of quinoline with PhNO₂ as oxidising agent. PhNO₂ appears to be reduced to NHPH·OH which becomes isomerised or condenses with CH₂:CH·CHO. H. W.

[Constitution of Knoevenagel's "acetone-anil." P. KALNIN (Ber., 1936, 69, [B], 2843; cf. A., 1936, 1123).—A reply to von Auwers (A., 1936, 1522). H. W.]

Quinone formation in the thalleioquinine reaction. Preparation of quinolyl-*o*-quinone. G. W. HARGREAVES (J. Amer. Pharm. Assoc., 1936, 25, 975—976).—6-Hydroxyquinoline (modified method of prep. described) with PbO₂ and H₂SO₄ yields quinolyl-*o*-quinone which, in common with oxidised solutions of quinine, gives a red solution when heated with NH₂Ph. The theory of quinone formation in the thalleioquinine reaction is thus supported (cf. A., 1926, 967). F. O. H.

Condensation of acetylene with aromatic amines. IV. Condensation with aniline and *p*-toluidine in presence of silver nitrate. N. KOZLOV and E. GIMPELEVITSCH. V. Condensation with *o*- and *p*-anisidine in presence of CuCl and HgCl₂. N. KOZLOV and R. BOGDANOVSKAJA. VI. Condensation with aniline in presence of HgCl₂, HgCl, and HgBr₂. N. KOZLOV, B. DINABURSKAJA, and T. RUBINA. VII. Condensation with aniline in presence of HgI₂. N. KOZLOV and R. PATSCHANOVA (J. Gen. Chem. Russ., 1936, 6, 1341—1345, 1346—1348, 1349—1351, 1352—1354).—IV. NH₂Ph and C₂H₂ in presence of AgNO₃ yield quinaldine (I) and tetrahydroquinaldine (II), whilst with *p*-toluidine the only identified product was 2:6-dimethylquinoline. The reaction consists probably of: NH₂Ph + C₂H₂ \rightarrow NPh:CHMe (III) : 2(III) \rightarrow NHPH·CHMe·CH:CH·NHPH (IV) \rightarrow NH₂Ph + (I) + H₂; (I) + 2H₂ \rightarrow (II).

V. *o*- or *p*-Anisidine and C₂H₂ in PhMe and CuCl yield 8-, m.p. 123—125°, or 6-methoxy-2-methylquinoline, b.p. 176—179°/33 mm. (methiodide, m.p. 229—230°); in presence of HgCl₂ in place of CuCl the respective products are diethylidene-*o*-, m.p. 102—103°, and -*p*-anisidine (cis- and trans-), m.p. 89° and 169°, which yield the appropriate quinaldines when heated.

VI. NH_2Ph and C_2H_2 in presence of HgCl , HgCl_2 , or HgBr_2 afford (IV), converted by heating into (I) and (II).

VII. The catalytic action of HgI_2 is identical with that of other Hg salts. R. T.

β -Hydroxyphenylethylamines and their transformations. IV. Synthesis of tetrahydroisoquinolinecarboxylic acids and the spontaneous decarboxylation of α -keto-acids under physiological conditions. G. HAHN and K. STEHL (Ber., 1936, 69, [B], 2627—2654).—The condensation of phenylethanolamines with α -CO-acids capable of enolisation to compounds,

$\text{C}_6\text{H}_3\text{X}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}(\text{OH})(\text{CH}_2\text{R})\cdot\text{CO}_2\text{H}$ occurs very readily if the energy liberated by saturation of the double linking is equiv. to that required for the detachment of H and depends greatly on the p_H of the solution. Subsequent ring-closure to an isoquinoline takes place if a nuclear H is sufficiently loosened by a substituent in the *para*-position; otherwise, decarboxylation occurs. The changes are usually concurrent to some extent but their rates differ greatly. β -3 : 4-Dihydroxyphenylethylamine (I) and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, best at p_H 6, yield 6 : 7-dihydroxy-1-benzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline-1-carboxylic acid, unstable to air (hydrochloride, decomp. about 240° after becoming yellow), converted by Me_2SO_4 and NaOH into Me 6 : 7-dimethoxy-1-benzyl-2-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline-1-carboxylate (II), m.p. 118° ; the corresponding acid (III), decomp. 179 — 181° after shrinking at 100° (hydrochloride, m.p. 199 — 200°), loses CO_2 when kept in diffused light, more rapidly in sunlight, giving a yellow oil insol. in alkali. The mother-liquors from (II) when treated with 50% KOH evolve Me_2O and give the methylbetaine, m.p. 138 — 139° (hydrochloride, decomp. 167°), of (III). AcCO_2H and (I) at about p_H 4 and 25° afford 6 : 7-dihydroxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline-1-carboxylic acid, decomp. 230 — 235° when heated moderately rapidly. (I) and $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ at p_H 5 yield 6 : 7-dihydroxy-1-p-hydroxybenzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline-1-carboxylic acid (hydrochloride, decomp. 260° after becoming discoloured at about 240°); at p_H 6.6 the reaction is greatly disturbed by atm. oxidation. 6 : 7-Dihydroxy-1-m-hydroxybenzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline-1-carboxylic acid and its hydrochloride, decomp. 255° after becoming discoloured at 220° , are obtained similarly. 6 : 7-Dihydroxy-1-o-hydroxybenzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline-1-carboxylic acid, decomp. $>250^\circ$ when heated moderately rapidly [hydrochloride (+ $3\text{H}_2\text{O}$), m.p. 155° , decomp. $>220^\circ$], is obtained at 100° . (I) and α -ketoglutaric acid do not react at 25° and p_H 3—6 and the lactam, decomp. 255 — 260° after darkening at 215° , of 6 : 7-dihydroxy-1-carbethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline-1-carboxylic acid is best obtained from the reactants at 100° and $p_H < 1$. 6 : 7-Dihydroxy-1-4'-hydroxy-3'-methoxybenzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline-1-carboxylic acid (+ H_2O), decomp. 230° after becoming yellow, and its hydrochloride (+ H_2O), decomp. 255 — 260° , are described. Reaction does not appear to take place between (I) and BzCO_2H or between adrenaline and AcCO_2H , AcCO_2Alk ,

$(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, MeCHO , or $\text{CH}_2\text{Ph}\cdot\text{CHO}$. If the OH of (I) are etherified, condensation with α -CO-acids proceeds only to the formation of Schiff's bases. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$ (IV) and AcCO_2H at 25° and p_H 4 readily evolve CO_2 (yield 65% calc. on amine) and give a red oil which could not be satisfactorily purified; the possibility that it is the Schiff's base from (IV) and MeCHO is strengthened by the analogous behaviour of these substances towards one another but the reaction is not simple. Under similar conditions, decarboxylation occurs, but at $p_H \sim 4$, but it is not immaterial whether this condition is secured by NaOH or NH_3 since the latter has a marked, proper decarboxylating action. The most favourable concn. of AcO_2H is 4M; the poorer results obtained at greater dilution are due to increased dissociation and consequently lessened enolisation. Higher temp. favours decarboxylation at the expense of possible side-reactions. In PhOH or glycerol reaction does not take place better than in H_2O ; in contrast with the carboxylase models of Langenbeck which are active only in absolutely anhyd. media, H_2O is without harmful effect. Variation in the α -CO-acid appears to have little influence on the change if enolisation is possible; otherwise CO_2 is not evolved. All primary amines (NH_3 , NH_2Me , NH_2Ph , $\text{CH}_2\text{Ph}\cdot\text{NH}_2$, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$, and histamine) are active whereas *sec.*-amines and NH_2 -acids (arginine, glutamic acid, tyrosine, tryptophan, Me clupearate) do not induce change. H. W.

Molecular compounds with sodium picrate. C. SCHÖPF, A. HARTMANN, and K. KOCH (Ber., 1936, 69, [B], 2766—2769).—The Na salt of glutacondialdehyde (purification described) is converted by successive treatment with NH_2Ph in HCl and picric acid into the 1-phenylpyridinium salt, $\text{C}_{17}\text{H}_{12}\text{O}_7\text{N}_4\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3\text{Na}$, m.p. 191 — 193° , obtained also from its components in EtOH. 2-Phenylisoquinolinium picrate, m.p. 125 — 127° after softening at 120° (prep. from homophthalaldehyde described), does not give an additive compound whereas isoquinoline 2-oxide affords the adduct, $\text{C}_9\text{H}_7\text{ON}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3\cdot 2\text{C}_6\text{H}_2\text{O}_7\text{N}_3\text{Na}$, m.p. 241 — 243° . H. W.

Polymembered cyclic compounds. IX. cycloDitridecamethylenedi-imine and tridecamethyleneimine. A. MÜLLER and A. F. SCHÜTZ [with, in part, R. TREER] (Ber., 1936, 69, [B], 2790—2792; cf. A., 1934, 419).—Attempts to oxidise *NN'*-dibenzoyl- (I) or *NN'*-dibenzenesulphonyl-cycloDitridecamethylenedi-imine were unsuccessful. (I) passes when heated with PBr_5 in high vac. into α -dibromo-*n*-tridecane, identified by conversion into α -diphenoxy-*n*-tridecane, m.p. 67 — 68° and, after re-solidification, m.p. 64.5 — 65° , and Me_2 *n*-tridecane- α -dicarboxylate, m.p. 42.7 — 43° (corr.). Tridecamethyleneimine aurichloride has m.p. about 160° . H. W.

isoCarbamides and isoureides. IV. Condensation of isocarbamides with ketones and ketonic esters. S. BASTERFIELD, A. E. BAUGHEN, and I. BERGSTEINSON (Trans. Roy. Soc. Canada, 1936, [iii], 30, III, 115—127; cf. A., 1929, 329).— Ac_2 and Bz_2 (1 mol.) with ethylisocarbamide (I) (2 mols.) afford diethylureido-diacetyl, m.p. 240°

(decomp.) (*dihydrochloride*), and *-dibenzoyl* (II), m.p. 245° (decomp.), respectively, converted through the hydrochlorides into the *diureides*, m.p. >300°. Equimol. amounts of (I) and Bz₂ in dry Et₂O afford an additive compound, m.p. 87°, converted at 90° into (II). (I) with BzCO₂Et affords *benzoylformylethylisocarbamide*, m.p. 163° (decomp.) (*oxime*, m.p. 188°; *semicarbazone*, m.p. 238°), and with CHPh(CO₂Me)₂ at 50° affords *2-ethoxy-5-phenylbarbituric acid*, m.p. 220° (*ethylisocarbamate*, m.p. 237°), hydrolysed (dil. HCl) to *5-phenylbarbituric acid*, m.p. 253°. (I) (2 mols.) with Et succinosuccinate (1 mol.) in anhyd. Et₂O at <0° affords an additive compound, m.p. 110° (decomp.), which when boiled in C₆H₆ is converted into 4:5':5:4'-*dimethylene-2:2'-diethoxydiuracil*, decomp. at 305° (*dihydrochloride*, decomposed at 100° into EtCl and 4:5':5:4'-*dimethylenediuracil*). (I) (2 mols.) with Me phenylformylacetate (III) (1 mol.) in dry Et₂O affords *2-ethoxy-5-phenyluracil*, m.p. 211°, converted through an unstable hydrochloride at 100° into *5-phenyluracil* (IV). Similarly, (III) with *cyclohexylisocarbamide* (V) in Et₂O affords *2-cyclohexyloxy-5-phenyluracil*, m.p. 171°, converted (HCl) into (IV). Me oxalacetate with (I) or (V) in dry Et₂O affords *Me ethylisocarbamidodioxalacetate* (?), m.p. 140°, and *Me cyclohexylisocarbamido-oxalacetate* (?), m.p. 131°, respectively. Neither product is cyclised when heated. J. L. D.

Attempted synthesis of gem-substituted 6:6-dihydrouracils. E. PHILIPPI, F. HENDGEN, and F. HERNLER (Monatsh., 1936, 69, 270—283).—Treatment of the appropriate ketone with Mg and CH₂Br·CO₂Me in C₆H₆ affords *Me β-hydroxy-β-methyl-n-valerate*, b.p. 67°/10 mm. (yield 58—60%), *Me β-hydroxy-β-ethyl-n-valerate*, b.p. 80°/11 mm., and *Me β-hydroxy-β-methyl-n-hexanoate*, b.p. 81°/12 mm., respectively. Cautious addition of the OH-esters in CCl₄ to PCl₅ in CCl₄ at >35° gives the following: *Me β-chloro-β-methyl-n-valerate*, b.p. 48°/16 mm. (yield 42%), *Me β-chloro-β-ethyl-n-valerate*, b.p. 58°/11 mm., *Me β-chloro-β-methyl-n-hexanoate*, b.p. 59°/13 mm., *Et β-chloro-β-methyl-n-valerate*, b.p. 54°/14 mm., *Et β-chloro-β-ethyl-n-valerate*, b.p. 68°/12 mm., and *Et β-chloro-β-methyl-n-hexanoate*, b.p. 67°/11 mm. Cautious treatment of these esters with NH₃ in cold EtOH gives *Me β-methyl-Δ^α-pentenoate*, b.p. 49.5°/11 mm., *Me β-ethyl-Δ^α-pentenoate*, b.p. 57°/11 mm., *Me β-methyl-Δ^α-hexenoate*, b.p. 57°/12 mm., *Et β-methyl-Δ^α-pentenoate*, b.p. 55°/11 mm., *Et β-ethyl-Δ^α-pentenoate* (I), b.p. 66°/11 mm., and *Et β-methyl-Δ^α-hexenoate*, b.p. 66°/11 mm. Treatment of Et β-methyl-Δ^α-butenoate with CO(NH₂)₂ in EtOH at 150° leads to 4:4-*dimethyldihydrouracil*, m.p. 202°, but the reaction cannot apparently be extended to other acrylates. (I) is transformed by NH₃-EtOH at 135—145° into a mixture of β-ethyl-Δ^β-pentenoamide, m.p. 116°, and *Et β-amino-β-methyl-n-hexoic acid* has m.p. 187°. (II) and PhNCO give β-phenylureido-β-ethyl-valeric acid, m.p. 145°. (II) is converted by aq.

KCNO at 100° into 4:4-*diethyldihydrouracil*, m.p. 188°, in minimal yield. 4-*Methyl-4-propyldihydrouracil* has m.p. 191°. H. W.

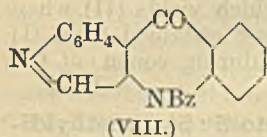
Active iron. IX. Reactions with 2:2'-di-pyridyl and o-phenanthroline.—See A., I, 94.

Preparation of 2-pyridyl-N-pyridinium derivatives. Z. RODEWALD and E. PŁĄZEK (Rocz. Chem., 1936, 16, 444—450).—C₅H₅N·HCl and CII are heated for 7 hr. at 250°, the mass is poured into aq. K₂CO₃, and steam-distilled. The residue is filtered and cooled, when 2-pyridyl-N-pyridinium iodide (I), m.p. 209° (*picrate*, m.p. 136°), is obtained. Alternatively, (I) is prepared from 2-iodopyridine and C₅H₅N·HCl (5 hr. at 240°). (I) and aq. NH₃ (8 hr. at 150°) afford 2-aminopyridine (II). (I) in H₂O and HI afford the *hydriodide* of 2-pyridyl-N-iodopyridinium iodide, m.p. 99°, which yields (II) when heated with aq. NH₃. The base obtained from (I) and Ag₂O rapidly decomposes during concn. of the solution. R. T.

Derivatives of 3:3'-diketo-5:5'-dimethyldihydro-2:2'-di-indolyl. A. WRÓBEL (Rocz. Chem., 1936, 16, 416—423).—Diacetyltartaric anhydride and *p*-toluidine (I) (1—2 hr. at 150°) yield 3:3'-*diketo-5:5'-dimethyldihydro-2:2'-di-indolyl* (II), m.p. 260° (decomp.). (II) and Br in EtOH afford 2:2':3'-*tribromo-3'-hydroxy-3-keto-5:5'-dimethyldihydro-2:2'-di-indolyl* (III), m.p. 221°, which eliminates Br when treated with H₂O, to yield the 2:2'-Br₂-derivative of (II), m.p. 74°. A by-product obtained together with (III) is αβ-di-*p*-tolyliminosuccinyl bromide, m.p. 227.5°, which with aq. KOH gives (I). Bromination of (II) in AcOH affords 2-(2'-bromo-3'-keto-5'-methyl-2:2'-indolyl)-3-keto-5-methylindolenine, m.p. 210°. (II) and HNO₃ afford 3:3'-*dinitro-2:3:2':3'-tetrahydroxy-5:5'-dimethyldihydro-2:2'-di-indolyl*, decomp. at 230°. R. T.

Derivatives of Py:Py'-tetrahydrodiquinolyl. A. WRÓBEL (Rocz. Chem., 1936, 16, 424—430).—Diacetyltartaric anhydride (I) and *o*-toluidine (2 hr. at 140—150°) afford 3:3'-*diketo-1:1':2:2':3:3':4:4'-tetrahydro-2:2'-diquinolyl* (II), m.p. 130°, which yields 2:3:2':3'-*tetrabromo-3:3'-dihydroxy-1:1':2:2':3:3':4:4'-tetrahydro-2:2'-diquinolyl* (III), m.p. 225° (decomp.), when brominated in AcOH. (III) is converted by H₂O into the 2:2'-Br₂-derivative, m.p. 48°, of (II). (I) and *o*-4-xylidine (5 hr. at 150°) yield 3-hydroxy-3'-keto-4-xylidino-6:6'-*dimethyl-1:1':2:2':3:3':4:4'-tetrahydro-2:2'-diquinolyl* (IV), m.p. 173°, which eliminates xylidine when heated with aq. KOH, to afford 3:4-*dihydroxy-3'-keto-6:6'-dimethyl-1:1':2:2':3:3':4:4'-tetrahydro-2:2'-diquinolyl*, m.p. 221°. (IV) and BzCl (at the b.p.) yield 3:3'-*diketo-6:6'-dimethyl-1:1':2:2':3:3':4:4'-tetrahydro-2:2'-diquinolyl*, m.p. 215°. (IV) and Br in EtOH afford 2:3:2':3'-*tetrabromo-3:3'-dihydroxy-4-xylidino-6:6'-dimethyl-1:1':2:2':3:3':4:4'-tetrahydro-2:2'-diquinolyl*, m.p. 228° (decomp.), converted by adding H₂O to its AcOH or EtOH solutions respectively into 2:2'-*dibromo-3:4-dihydroxy-3'-keto-4-xylidino*, m.p. 43°, and 2:2'-*dibromo-4-hydroxy-3:3'-diketo-6:6'-dimethyl-1:1':2:2':3:3':4:4'-tetrahydro-2:2'-diquinolyl*, m.p. 43°. R. T.

Benzoyl derivatives of indigotin. III. H. DE DIESBACH and T. DOBBELMAN (Helv. Chim. Acta, 1936, 19, 1213—1222; cf. A., 1934, 306).—Evidence is adduced in favour of the view that the formation of Dessoulavy's compound (I), Höchst Yellow R (II) and U (III), and Indigo Yellow 3G Ciba (IV) from indigotin (V) and BzCl involves successive ring-closure between the Ph of BzCl and the median C of (V), formation of new rings under the influence of BzCl, and oxidation. Formation of (I) in boiling BzCl uses 4 mols. of BzCl. Di- (VI), but not tetra-benzoyl-indigotin (VII), m.p. 242—243° (modified prep.; 75% yield), gives (I) in boiling BzCl. (VI), BzCl, and a little Cu in PhNO₂ at 160° give (II). (VII), BzCl (or *p*-C₆H₄Cl·COCl or C₅H₁₁·COCl), and a little Cu in PhNO₂ or C₆H₄(NO₂)₂ (not C₆H₃Cl₃) at 160° (not 120°) give a substance, C₃₀H₂₀N₄O₄, m.p. 384°, which is believed to be (VIII), because



with NaOH at 300° it gives *o*-NH₂·C₆H₄·CO₂H (1 mol.) and BzOH (2 mols.), with hot KOH-EtOH it gives *o*-NHBz·C₆H₄·CO₂H and a substance, m.p. 190° (? an impure isomeride), with conc. HCl at 200° gives 2 mols. of BzOH and a small amount of another substance, is stable to H₂SO₄ at 200°, and with AlCl₃-NaCl at 170° affords (III). (II) and AlCl₃-NaCl at 170° give (III). (I), BzCl, and a little Cu in PhNO₂ at 150—160° give 20% of (IV), 4 mols. of BzCl being used; in the absence of Cu a mixture of (I) and (II) is obtained; in C₆H₃Cl₃ at 160° (II) is formed, but addition of a little NaNO₂ or passage of O₂ gives 21—27% of (IV) with little or no (II). R. S. C.

3:4-Pyridopyrazine and a pyridylbenzotriazole. E. KOENIGS, H. BUEREN, and G. JUNG (Ber., 1936, 69, [B], 2690—2695; cf. A., 1924, i, 988).—Reduction of 4-nitroaminopyridine in acid solution affords a complex mixture of bases from which 4-chloro-, 4-amino-, and 4-hydrazino-pyridine have been isolated; there is no evidence of the production of 3:4-diaminopyridine (I), m.p. 218—219° (*picrate*, m.p. 235—237°; *platinichloride*, gradual decomp. >200°; Bz₂ derivative, m.p. 222—223°, and its *picrate*, m.p. 251°), which is readily obtained by reduction of 3-nitro-4-aminopyridine by aq. Na₂S at 80°. (I) and glyoxal Na H sulphite (II) in aq. AcOH at 100° give a colourless compound which loses SO₂ when heated giving 3:4-pyridopyrazine, C₅H₃N₃ $\begin{smallmatrix} \text{N}:\text{CH} \\ \text{N}:\text{CH} \end{smallmatrix}$ m.p. 100—101° (*picrate*, decomp. 185° after blackening at >130°). (I) and phenanthraquinone in boiling AcOH afford *phenanthra*-3:4-pyridopyrazine, m.p. 254° after softening (*picrate*, decomp. 262—263° after softening and becoming discoloured). 6-Chloro-3:4-pyridopyrazine, m.p. 138—139° (*hydrochloride*, decomp. >250°), is obtained from (II) and 6-chloro-3:4-diaminopyridine. 4-Chloropyridine and *p*-OMe·C₆H₄·NH₂ at 180° give 4-*p*-anisylaminopyridine, m.p. 172° (*picrate*, m.p. 179°), converted by aq. HNO₃ containing HNO₂ at 100° into 4-2'-nitro-4'-methoxyanilinopyridine, m.p. 186°, reduced by aq. Na₂S at 70° to 4-2'-amino-4'-methoxyanilinopyridine (III), m.p. 138°. Diazotisation of (III) in 2N-H₂SO₄ leads to 5-methoxy-1-4'-pyridylbenzotriazole, m.p. 165°. H. W.

Absorption of light and tautomerism of uric acids. H. BILTZ (Ber., 1936, 69, [B], 2750—2752).—The optical investigations of Fromherz *et al.* (this vol., 36) do not afford any proof that the acid position of the uric acid ion is at N₉ and do not controvert the author's view, based on chemical observations, that it is at C₈. H. W.

Potentiometric study of flavins.—See A., I, 85.

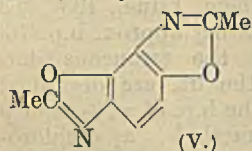
Phthalocyanines. VII. Phthalocyanine as a co-ordinating group. Metallic derivatives. P. A. BARRETT, C. E. DENT, and R. P. LINSTEAD. VIII. 1:2-Naphthalocyanines. E. F. BRADBROOK and R. P. LINSTEAD (J.C.S., 1936, 1719—1736, 1744—1748).—VII. The prep. and properties of the following derivatives of phthalocyanine are described: Na₂, K₂, Ca, Be (+2H₂O), Mg, Zn, Cd, Ni, Pb, Co, chloroaluminium, hydroxoaluminium (+H₂O), Sn^{II} and Sn^{IV}, dichloro- and di-iodo-tin, Pt^{II}, Fe^{II}, Mn^{II}, and V phthalocyanine; Zn, Co, chloroaluminium (+2H₂O), hydroxoaluminium, and dichlorotin chloro-phthalocyanine; Al phthalocyanine oxide; K salt of dihydroxotin phthalocyanine; Sn^{II} phthalocyanine hydrochloride and dichlorotin chlorophthalocyanine. Phthalocyanine acts throughout as a bivalent unit capable of occupying four positions in the co-ordination sphere of a metal. The changes undergone by metallic reagents in their efforts to accomplish the formation of phthalocyanine derivatives from N derivatives of phthalic acid are discussed.

VIII. Only 1:2- and 2:3-C₁₀H₆(CN)₂ yield phthalocyanine-like compounds. The 1:2-naphthalocyanines possess a general similarity to the corresponding phthalocyanines but isomerism occurs and isolation of cryst. compounds is difficult. The following are described: Cu and Pb 1:2-naphthalocyanine; Cu chloro-1:2-naphthalocyanine; α- and β-Mg 1:2-naphthalocyanine (+H₂O); α- and β-1:2-naphthalocyanine. F. R. S.

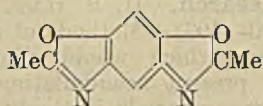
Stereochemistry of metallic phthalocyanines. R. P. LINSTEAD and J. M. ROBERTSON (J.C.S., 1936, 1736—1738).—X-Ray measurements on Be, Mn, Fe, and Co phthalocyanines are described. The crystals are closely isomorphous and their mol. dimensions are practically identical; all have centro-symmetrical mols. The stereochemical implications are discussed. F. R. S.

Benzoxazole series. K. FRIES and F. BEYERLEIN (Annalen, 1936, 527, 71—83).—Benzoxazole, like benziminazole and benzthiazole, is intermediate in character between the benzenoid and naphthoid systems. Nitroresorcinol is heated in Ac₂O containing Co-Ni-Cu under H₂ at high pressure at 150°, the product is treated with anhyd. NaOAc, and the acetamidoresorcinol is heated until Ac₂O ceases to be evolved, thereby giving 5-hydroxy-1-methylbenzoxazole (I) in about 70% yield. Chlorination of (I) in AcOH at room temp. affords 6-chloro-5-hydroxy-1-methylbenzoxazole (II), m.p. 211°, or, if more Cl₂ is used, 4:6-dichloro-5-hydroxy-1-methylbenzoxazole (III), m.p. 185°; further chlorination causes separation of NH₄Cl. Even with >2 Br 4:6-dibromo-5-hydroxy-1-methylbenzoxazole (IV), m.p. 202°, is formed in AcOH containing NaOAc. Nitra-

tion of (I) in AcOH at room temp. yields 4 : 6-dinitro-5-hydroxy-1-methylbenzoxazole, m.p. 208° (decomp.). Nitration of (II) and (IV) proceeds in the same manner as with benzenoid systems, giving 6-chloro-4-nitro-5-hydroxy-1-methylbenzoxazole, m.p. 247° (decomp.) (Na salt), also obtained from (IV), and 6-bromo-4-nitro-5-hydroxy-1-methylbenzoxazole, m.p. 238°. (I) couples with diazotised $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ to 5-hydroxy-1-methylbenzoxazole-6-azobenzene- p -sulphonic acid (Na salt), reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in $2\text{N-Na}_2\text{CO}_3$ to 6-amino-5-hydroxy-1-methylbenzoxazole, m.p. 163°. This is transformed by boiling Ac_2O and subsequent heating at 210° into 2' : 2''-dimethyl-1 : 2 : 5 : 6-benzo-5' : 4' : 5'' : 4''-dioxazole (V), m.p. 109°. 4 : 6-Diacetamidoresorcinol diacetate passes at 320° into lin-2' : 2''-dimethyl-1 : 2 : 4 : 5-benzo-5' : 4' : 4'' : 5''-dioxazole (VI), m.p. 143°. (VI) is more readily hydrolysed than (V) by dil. acids and the heat of combustion



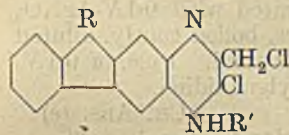
(V.)



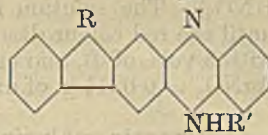
(VI.)

of (V) is about 1.3 kg.-cal. per mol. > that of (VI). Nitrohydroxyquinol triacetate is converted by treatment with H_2 under high pressure at 150° in Ac_2O containing Co-Ni-Cu followed by anhyd. NaOAc into the Ac_4 , m.p. 188°, and Ac_5 , m.p. 136°, derivatives of 2 : 4 : 5-trihydroxyaniline; the mixture passes at 250° into 4 : 5-dihydroxy-1-methylbenzoxazole, m.p. 231° after darkening at 225° (diacetate, m.p. 103°), which could not be oxidised to an o -quinone by HNO_3 , CrO_3 , PbO_2 , or Ag_2O . 3 : 6-Dibromo-4 : 5-dihydroxy-1-methylbenzoxazole, m.p. 188° (hydrobromide), does not yield an o -quinone. H. W.

Synthesis of nitrogen-containing polycyclic compounds. I. C. FELDMAN (J. Gen. Chem. Russ., 1936, 6, 1234—1242).—2-Aminodiphenylene oxide (I) and $\text{CH}_2\text{Cl}\cdot\text{COCl}$ yield 2-chloroacetamido-diphenylene oxide [-dibenzfuran], m.p. 162—164°, converted by treating with PCl_5 and POCl_3 into the substance (II) ($\text{R} = \text{O}$, $\text{R}' = 2$ -dibenzfuryl), m.p. 240—242°. The corresponding substance (II) ($\text{R} = \text{CH}_2$, $\text{R}' =$



(II.)

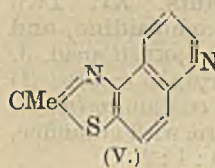


(V.)

2-fluorenyl), m.p. 238—239°, is obtained similarly from 2-chloroacetamidofluorene (III), m.p. 183—185°. (I) and pimeryl dichloride (IV) yield the di-2-diphenylene oxide derivative of pimelamide, m.p. 264—265°, which is condensed as above to afford the substance (V) ($\text{R} = \text{O}$, $\text{R}' = 2$ -dibenzfuryl), m.p. >300°, and similarly the 2-fluorenyl derivative of pimelamide, m.p. >300° [from (III) and (IV)] gives the substance of formula (V) ($\text{R} = \text{CH}_2$, $\text{R}' = 2$ -fluorenyl). R. T.

Benzthiazole. K. FRIES and A. WOLTER (Annalen, 1936, 527, 60—71).—Benzthiazole represents a transitional stage between a benzenoid and naphthoid system. 4-Bromo-5-nitroveratrole is converted by

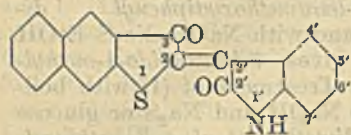
$\text{Na}_2\text{S-S}$ in boiling EtOH into 2 : 2'-dinitro-4 : 4' : 5 : 5'-tetramethoxydiphenyl disulphide, m.p. 227°, transformed by the successive action of Sn-HCl and BzCl into 5-benzamido-4-benzoylthiolveratrole, m.p. 153°, which with conc. H_2SO_4 at room temp. affords 2 : 2'-dibenzamido-4 : 4' : 5 : 5'-tetramethoxydiphenyl disulphide (I), m.p. 175°, and with $\text{NaOH-Na}_2\text{S-EtOH}$ followed by Me_2SO_4 gives 5-benzamido-4-methylthiolveratrole, m.p. 87°. Treatment of (I) with boiling HCl-AcOH or with NaOH and Na_2S or glucose in EtOH leads to 4 : 5-dimethoxy-1-phenylbenzthiazole (II), m.p. 152° [monohydrochloride, m.p. 180° (decomp.)], decomposed by cold H_2O into (II); trihydrochloride, m.p. 244° (decomp.), which gives (II) by long treatment with boiling H_2O . (II) is demethylated by boiling 60% H_2SO_4 to 4 : 5-dihydroxy-1-phenylbenzthiazole, m.p. 292° (Ac_2 derivative, m.p. 154°), which could not be oxidised to an o -quinone by HNO_3 , CrO_3 , PbO_2 , Ag_2O , Pb(OAc)_4 , or I and is converted by Br in boiling AcOH into 3 : 6-dibromo-4 : 5-dihydroxy-1-phenylbenzthiazole, m.p. 195° (diacetate, m.p. 214°), from which an o -quinone could not be derived. 4-Nitro-1-methylbenzthiazole, m.p. 139°, obtained from 4-nitro-2-aminothiophenol and Ac_2O or, preferably, by the action of $\text{Na}_2\text{S-S}$ on 2-bromo-5-nitroacetanilide in boiling EtOH, is reduced by Sn and fuming HCl in presence of EtOH to 4-amino-1-methylbenzthiazole (III), m.p. 102° (Ac derivative, m.p. 157° or m.p. 125° and m.p. 156° after re-solidification if crystallised from EtOH), which could not be condensed with PhCHO . Chlorination of (III) in AcOH containing HCl followed by treatment with $\text{SnCl}_2\text{-AcOH}$ leads to 3 : 5 : 6-trichloro-4-hydroxy-1-methylbenzthiazole, m.p. 158° (acetate, m.p. 92°), oxidised by HNO_3 (d 1.4) in AcOH at 100° to 5 : 6-dichloro-1-methylbenzthiazole-3 : 4-quinone (IV), m.p. 178°, which with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives a quinoxaline derivative, m.p. 270°. (IV) is reduced by SO_2 to 5 : 6-dichloro-3 : 4-dihydroxy-1-methylbenzthiazole, m.p. 225° (diacetate, m.p. 176°). (III) passes by Skraup's reaction into 2'-methyl-4' : 5'-thiazolo-5 : 6-quinoline (V), m.p. 108° (sulphate; hydrochloride; double compound with HgCl_2); the corresponding meliodide, decomp. 265° after darkening at 250°, is oxidised by $\text{K}_3\text{Fe(CN)}_6$ in alkaline solution to 2-keto-2'-methyl-4' : 5'-thiazolo-1-methyl-1 : 2-dihydro-5 : 6-quinoline, m.p. 217°. 3-Chloro-4-acetamido-1-methylbenzthiazole, m.p. 154°, is hydrolysed by boiling conc. HCl to 3-chloro-4-amino-1-methylbenzthiazole, m.p. 124°, which is converted into 8-chloro-2'-methyl-4' : 5'-thiazolo-6 : 7-quinoline, m.p. 170° (hydrochloride; unstable mercurichloride), in very small yield. Acet- p -nitroanilide is converted by $\text{P}_2\text{S}_5\text{-K}_2\text{S}$ in boiling PhMe into thioacet- p -nitroanilide, m.p. 175°, which could not be oxidised by $\text{K}_3\text{Fe(CN)}_6$ in alkaline solution to the corresponding benzthiazole. H. W.



(V.)

Dyes derived from isatin. Azines and indigoid vat dyes. S. K. GUHA and H. BASU-MALLICK (J. Indian Chem. Soc., 1936, 13, 571—574).—Isatin when boiled with 2 : 3-diaminoacenaphthene in AcOH yields acenaphthenoindazine, m.p. >310°. Ace-

naphtheno-5-nitro- and -5:7-dinitro-indazine (both sublime above 310°) were similarly prepared from the appropriate substituted isatin. These azines dye wool various shades of yellow. The following compounds were prepared by treating 4:5-benzo-oxythio-



nitro-, and 5:7-dinitro-3-(4':5'-benzo-oxythionaphthylidene)oxindole. They melt above 395°, form deep yellow vats, and dye cotton various shades of violet. The general formula is annexed. H. G. M.

Tobacco alkaloids. IX. Syntheses of *l*- and *d*-nornicotine. E. SPÄTH and F. KESZLER (Ber., 1936, 69, [B], 2725—2727).—Successive treatments of *r*-nornicotine in MeOH with *l*- and *d*-6:6'-dinitro-2:2'-diphenic acid and purification of the crude optically active bases through their perchlorates lead to *l*- and *d*-nornicotine. H. W.

Synthesis of local anaesthetics from cytosine. H. R. ING and R. P. PATEL (J.C.S., 1936, 1774—1775).—Cytosine and (CH₃)₂O give *N*-β-hydroxyethylcytosine (+H₂O), m.p. 73—74°, which with the appropriate reagent affords β-cytisinooethyl benzoate, m.p. 247—248° (decomp.), and cinnamate hydrobromides, m.p. 246—247° (decomp.). γ-Chloropropyl benzoate, NaI, and cytosine, followed by KBr, yield γ-cytisinopropyl benzoate hydrobromide, m.p. 232—233° (decomp.), and hydrobromides of the following have been similarly prepared: cinnamate, m.p. 224—225° (decomp.), phenylcarbamate, m.p. 225—226° (decomp.), α-naphthylcarbamate, m.p. 237—238°, *p*-nitrobenzoate, m.p. 255—256°, *p*-aminobenzoate (I), m.p. 236—237°, *p*-Cytisinooethyl *p*-nitrobenzoate, m.p. 103—104° (hydrobromide, m.p. 232—233°), and γ-cytisinopropyl α-naphthylcarbamate, m.p. 159°, are also described. All except (I) possess local anaesthetic properties. F. R. S.

Alkaloids of fumariaceous plants. XI. Two new alkaloids, corlumine and corluminine, and their constitutions. R. H. F. MANSKE (Canad. J. Res., 1936, 14, B, 325—327).—*Corydalis scouleri* (I) and *sibirica* and *Dicentra cucullaria* contain corlumine (II), m.p. 158°, which is stereoisomeric with adlumine, since it is hydrolysed to lodal and 3:4:2-CH₂O₂:C₆H₂(CO₂H):CHO (best identified by conversion by aq. alkali into 3:4-methylenedioxy-phthalic acid and -phthalide). (I) contains also corluminine, m.p. 236° [a phenolic base, converted into (II) by CH₂N₂], and 2:9-dihydroxy-3:10-dimethoxytetrahydroprotoberberine. R. S. C.

Alkaloid from *Equisetum palustre*. E. GLET, J. GUTSCHMIDT, and P. GLET (Z. physiol. Chem., 1936, 244, 229—234).—The plant yields a hydrocarbon, C₂₁H₄₂, m.p. 77° and a mixture of H₂O-sol. bases, including palustrine, C₁₂H₂₄O₂N₂ (I), b.p. 205—210°/0.1 mm. (hydrochloride, m.p. 181°). Shoots collected in June contain 0.95% of their dry wt. of (I). W. McC.

Solanidine-*t* and -*s*. H. ROCHELMAYER (Arch. Pharm., 1936, 274, 543—545).—Dehydrogenation of solanidine-*t* (cf. A., 1936, 216) and (probably) -*s* (Se; 320°) gives methylcyclopentanophenanthrene. R. S. C.

Organic magnesium compounds. III. Lead tris-*m*-tolyl. IV. Reaction between alkyl *p*-toluenesulphonates and RO·Mg·X. K. MINE (J. Chem. Soc. Japan, 1934, 55, 1168—1173).—III. Pb(C₆H₄Me-*m*)₃ is prepared from *m*-C₆H₄Me·MgBr and PbCl₂.

IV. The reaction is 2C₆H₄Me·SO₃R' + 2RO·MgX → (C₆H₄Me·SO₃)₂Mg + (RO)₂Mg + 2R'X.

CH. ABS. (r)

Base-protein-acid compounds.—See A., III, 56.

Estimation of b.p. as an aid in organic research. H. B. HASS (J. Chem. Educ., 1936, 13, 490—493).—Methods of calculating approx. b.p./760 mm. which would eliminate the erroneous data at present accumulating in the lit. are described. Erroneous vals. in the lit. for the b.p. of α-, β-, and γ-chloropentane, αγ-dichloro-β-methyl-, αγ-dichloro-, and α-nitro-β-methyl-propane, αδ-dichlorobutane, and Δ⁴-pentene are corr. L. S. T.

New heating vessel for the Pregl micro-desiccator. JENAER GLASWERK, SCHOTT U. GEN. (Mikrochem., 1936, 21, 131—132).—The heating reservoir of the apparatus is formed by an annular glass space, heating being carried out through the centre. J. W. S.

Determination of diphenylguanidine. S. MINATOYA, T. EBE, and I. AOI (J. Soc. Rubber Ind. Japan, 1935, 8, 328—337).—A 0.5-g. sample is heated on a water-bath under reflux for 20 hr. with 0.2 g. of CaO, 30 c.c. of abs. EtOH, and 3 c.c. of CS₂. The product is added to 250 c.c. of hot H₂O and evaporated to dryness. To the residue are added 30 c.c. of a solution (A) of 5 g. of Fe in 60 c.c. of conc. HNO₃, which has been evaporated to a syrup and diluted to 500 c.c. Fe(CNS)₃ is formed. The product is heated gently, and made up to 100 c.c. by solution B (500 c.c. of H₂O + 30 c.c. of solution A and 5 c.c. of conc. HNO₃). The solution is titrated with 0.1N-AgNO₃ until the red colour disappears, boiled gently, diluted with 3 vols. of B, and again titrated. 1 c.c. of 0.1N-AgNO₃ = 0.0211 g. of diphenylguanidine.

CH. ABS. (e)

Systematic analysis of anions.—See A., I, 96.

Reactions with nitroprusside of reduced glutathione, cysteine, acetone, and creatinine.—See A., III, 8.

Preparation of extremely pure liquids. W. SWIENTOSLAWSKI (Svensk Kem. Tidskr., 1936, 48, 257—265).—The liquid is distilled up seven fractionating columns in cascade at a measured rate. The degree of purity is shown at each stage by the difference between the ebullition and condensation temp. The distribution of impurities is discussed.

M. H. M. A.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

MARCH, 1937.



Atomic interchange between water and saturated hydrocarbons.—See A., I, 143.

Action of oxygen in polymerisation reactions.—See A., I, 141.

Reversible catalytic conversion of *n*-butylenes into isobutylene. A. V. FROST, D. M. RUDKOVSKI, and E. K. SEREBRЯKOVА (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 373—376).—Quant. conversion of *n*-butylenes into isobutylene (I) in presence of six different catalysts is examined at about 300° and equilibrium relationships are determined between 265° and 426°. SiO₂ gel-H₃PO₄ promotes the largest yield (44.5%) of (I). F. N. W.

Influence of structure of olefines on the iodine value. S. LANDA and M. HABADA (Chem. Listy, 1937, 31, 4—10).—The I vals. obtained for Δ^α-hexadecene (I), β-methyl-Δ^β-heptadecene (II), and γ-ethyl-Δ^β-octadecene (III) are unaffected by varying the duration of reaction from 0.5 to 24 hr. In presence of excess of reagent normal I vals. are obtained for (I) and (II) (methods of Hübl and of Hanus), and abnormally high vals. for (III), δ-propyl-Δ^γ-nonadecene, ε-butyl-Δ^δ-eicosene, αα-diphenyl-Δ^α-hexadecene, and δμ-diethyltetradecane-Δ^{βγ}-diene. The I vals. are at a max. for the freshly prepared olefines, and fall more rapidly with time for dienes than for mono-olefines. It is concluded that the I val. is not of great val. in the analysis of mineral oils. R. T.

Carbon tetrachloride as a physico-chemical standard. A. ZMACZYNSKI (Svensk Kem. Tidskr., 1936, 48, 268—273; cf. this vol., 80).—The prep. of very pure CCl₄ is described. M. H. M. A.

Action of elementary fluorine on organic compounds. III. Vapour-phase fluorination of hexachloroethane. W. T. MILLER, jun., J. D. CALFEE, and L. A. BIGELOW (J. Amer. Chem. Soc., 1937, 59, 198—199; cf. A., 1934, 62).—C₂Cl₆ and F₂ react in the vapour phase over a heated Cu-gauze catalyst, yielding 20% of *s*-C₂Cl₄F₂. C₂Cl₄ yields the same product under similar conditions. E. S. H.

Preparation of α-chloro-γ-bromopropane, and the velocity of addition of HBr to allyl chloride. L. I. ANTZUS (J. Appl. Chem. Russ., 1936, 9, 2053—2054).—In disagreement with Schostakovski (A., 1936, 819), the sole product given by CH₂:CH·CH₂Cl and HBr at −19° to 0° is CHMeCl·CH₂Br. R. T.

Addition of hydrogen bromide to allyl bromide in the presence of various substances. III. Elucidation of the so-called peroxide effect. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1936, 11, 798—801; cf. this vol., 43).—

Allyl bromide (I) and O₂ form peroxides in light, but not in the dark; in presence of Pd-black no peroxides are formed even in the light. Peroxides present in (I) are destroyed by Pd-black. (I) liberates Br from HBr in presence of O₂ and Pd-black, but not of either alone. O₂, HBr, and Pd-black liberate Br without the presence of (I). The proportion of isomerides in a C₃H₅Br₂ mixture does not change in presence of O₂, Pd-black, and HBr. Thus, the "peroxide effect" is probably due to liberation of O₂ from peroxides rather than to the presence of the latter. R. S. C.

γ-Chloro-β-methyl-Δ^α-propene. O. SCHALES (Ber., 1937, 70, [B], 116—121).—γ-Chloro-β-methyl-Δ^α-propene (I) is shown to be a reactive substance. When boiled with 25% KOH-MeOH for 1 hr. (I) gives a 90% yield of CH₂:CMe·CH₂·OH and a 51% yield when heated with aq. K₂CO₃ at 100°. With Mg in Et₂O it readily affords βε-dimethyl-Δ^{αα}-hexadiene, b.p. 136—137°/760 mm. With PhOH and K₂CO₃ in boiling COMe₂ (I) yields *Ph* β-methyl-Δ^β-propenyl ether, b.p. 89°/10 mm. (yield 72%), which is isomerised in boiling NPhEt₂ to *o*-β-methyl-Δ^β-propenylphenol (II), b.p. 102—103°/11 mm. (*Me* ether, b.p. 92.5—94°/11 mm.). Treatment of (II) with boiling AcOH and 48% HBr yields polymerised products, but under mild conditions *dimethylcoumaran*, b.p. 198—204°/755 mm., 82—83°/16 mm., appears to result. Addition of (I) and NaOAc in EtOH-H₂O to a solution of barbituric acid at 70—73° gives 5:5-di-β-methyl-Δ^β-propenylbarbituric acid, m.p. 222°, the physiological action of which does not differ considerably from that of the homologous diallyl-barbituric acids. H. W.

Allyl change: a trichloroisobutene. A. KIRRMANN and R. JACOB (Compt. rend., 1936, 203, 1528—1529).—ααα-Trichloro-β-methylpropan-β-ol with P₂O₅ at 150° affords ααγ-trichloro-β-methyl-Δ^α-propene (I), b.p. 46°/12 mm. (which with KMnO₄-COMe₂ affords COMe·CH₂Cl), probably formed by the isomerisation of ααα-trichloro-β-methyl-Δ^β-propene (II). Analogues of (I) and (II) are prepared; one Cl of the former is much less reactive than in the latter. (I) with NaOAc gives an *acetate*, b.p. 79°/12 mm., hydrolysed to γγ-dichloro-β-methylallyl alcohol, b.p. 78—79°/13 mm. [*p*-nitrobenzoate, m.p. 91°, obtained also from (II) directly]. J. L. D.

Elimination of hydrogen chloride from βδ-dichloro-Δ^β-butene. II. A. L. KLEBANSKI, K. K. TSCHEVITSCHALOVA, and A. P. BELENKAJA (J. Appl. Chem. Russ., 1936, 9, 1985—1993).—Chloroprene is obtained in 65—70% yield by passing CHMeCl:CH·CH₂Cl (I) over CaCl₂ on Cu turnings at

350—400°, or by passing 1:1 steam-(I) mixtures over Cu, also at 350—400°. The inactivated catalysts are regenerated by heating in air at 500—550° for 3—4 hr. R. T.

Chloro-derivatives of aliphatic hydrocarbons. II. Allylic isomerisation of isopentenyl chlorides. D. V. TISCHTSCHENKO. **III. Chlorination of $\alpha\beta$ - and $\beta\gamma$ -dichlorobutanes.** D. V. TISCHTSCHENKO and A. TSCHURBAKOV (J. Gen. Chem. Russ., 1936, 6, 1549—1552, 1553—1558; cf. this vol., 2).—II. $\text{CH}_2\text{:CMe:CHMeCl}$ or $\text{CHMe:CMe:CH}_2\text{Cl}$ yield, when hydrolysed with H_2O at 70°, a mixture of COMePr^β , $\text{OH}\cdot\text{CHMe:CMe:CH}_2$ (α -naphthylurethane, m.p. 91.5—93°), and $\text{OH}\cdot\text{CH}_2\cdot\text{CMe:CHMe}$ (α -naphthylurethane, m.p. 103°). The alcohols afford isoprene when passed over MgSO_4 at 230—260°.

III. $\alpha\beta$ - or $\beta\gamma$ -Dichlorobutane and Cl_2 yield a mixture of $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CHMeCl}$ (I) and $\text{CHMeCl}\cdot\text{CMeCl}_2$ (II). (I), when distilled from KOH, yields a mixture of cis-, b.p. 134—136°, and trans- $\alpha\beta$ -dichloro- Δ^2 -butene, b.p. 101—103°, whilst (II) gives a mixture of cis-, b.p. 125—127°, and trans- $\beta\gamma$ -dichloro- Δ^2 -butene, b.p. 116—118°. The position of the Cl in the dichlorobutenes is determined by examining the products of ozonolysis. R. T.

Aliphatic chloro-derivatives. IV. Chlorination of isopentane. M. DAVIDOVA, Z. PANKINA, and D. TISCHTSCHENKO. **V. Catalytic decomposition of $\beta\gamma$ -dichlorobutane in presence of steam.** R. GUTNER and D. TISCHTSCHENKO (J. Gen. Chem. Russ., 1936, 6, 1615—1623, 1729—1735).—IV. All four possible monochloroisopentanes are obtained by chlorination at 18—20° in the liquid or gaseous phase.

V. $(\text{CHMeCl})_2$ (I) and H_2O [14 mols. of H_2O per mol. of (I)] at 360—400°, in presence of MgCl_2 - or $\text{CaCl}_2\cdot\text{SiO}_2$, give butadiene (II) in 35—38, CHMe:CMeCl (III) in 21—25, and COMeEt in 6—8% yield; the yield of (II) falls with increasing concn. of (I) in the mixture. In absence of H_2O the products are (III) and $(\text{CHMe})_2$, with $\geq 4\%$ of (II). Under similar conditions (III), $(\text{OH}\cdot\text{CHMe})_2$, or $\text{OH}\cdot\text{CHMe:CHMeCl}$ (IV) yields only traces of (II), which is the chief product obtained from $\text{CHMeCl}\cdot\text{CH:CH}_2$ (V) or $\text{CHMe:CH}\cdot\text{CH}_2\text{Cl}$ (VI) and H_2O . The probable reactions are $(\text{III}) \leftarrow (\text{I}) \rightarrow (\text{V}) \rightleftharpoons (\text{VI}) \rightarrow (\text{II})$; or $\text{COMeEt} \leftarrow (\text{IV}) \leftarrow (\text{I}) \rightleftharpoons (\text{VI}) \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CH:CHMe} \rightleftharpoons \text{OH}\cdot\text{CHMe:CH:CH}_2 \rightarrow (\text{II})$. R. T.

Determination of ethyl alcohol by a capillary-rise method. F. TODD (Amer. J. Pharm., 1936, 108, 488—497).—A method for the determination of EtOH in aq. solution is described. F. N. W.

$\beta\beta\beta$ -Tribromoethyl alcohol. F. DE CARLI and A. MANGINI (Atti V Congr. Naz. Chim., 1936, 14, 741—758).—In an attempt to prepare more stable derivatives of Avertin and to establish the function of the alcohol group, the following have been synthesised, and their solubility and physiological activity on the guinea-pig determined: $\beta\beta\beta$ -tribromoethyl benzoate, m.p. 35.5—36.5°, o-, m-, and p-nitrobenzoates, m.p. 117—118°, 82.5—83°, 100—101°, and carbonate, m.p. 112—113°; $\beta\beta\beta$ -tribromoethylphenylurethane, m.p. 107—108° (Chechik, A., 1932, 367,

gives m.p. 66—67°), $\beta\beta\beta$ -tribromoethyl-p-bromophenylurethane, m.p. 116—117°, di- $\beta\beta\beta$ -tribromoethyl-p-phenylenedi-, m.p. 239—240°, ethylenedi-, m.p. 102—103°, and o-, m-, and p-carboxyphenylurethane, m.p. 174—176°, 185—186° (partial decomp.), and 220—222° (decomp.). The results show that the narcotic activity is a sp. function of the alcoholic OH and the derivatives prepared have not the power of regenerating, by scission in the organism, the active principle. The derivatives are markedly lipo-sol. but this is not sufficient to permit narcotic activity without H_2O -solubility. L. A. O'N.

Hydrogenation of binary organic mixtures. I. Hydrogenation of mixtures of allyl alcohol and oleic acid. V. V. IPATIEV, jun., and I. F. BOGDANOV (J. Gen. Chem. Russ., 1936, 6, 1651—1658).—Hydrogenation (Pt catalyst) of oleic acid does not commence until that of allyl alcohol is completed. R. T.

Selective hydrogenation of unsaturated esters to unsaturated alcohols. J. SAUER and H. ADKINS (J. Amer. Chem. Soc., 1937, 59, 1—3).—Bu oleate with H_2 (200 atm.) and a large amount of a Zn-Cr oxide catalyst (I) at 300° gives 65% of octadecanol, b.p. 158°/2 mm. (containing 13% of octadecanol); with less (I) at 282°, octadecenyl oleate, b.p. 272°/1 mm., is also formed. Similarly, Bu Δ^1 -undecenoate, b.p. 116°/2 mm., affords 37% of undecanol, b.p. 133°/16 mm. (containing 9% of undecanol), whilst Bu Δ^1 -erucate, b.p. 211—212°/1 mm. (by butanolysis of rape-seed oil), gives 68% of docosenol, b.p. 196°/3 mm., m.p. 34—35° (containing 3% of docosanol). Zn-V oxide and Zn-Mo oxide catalysts are inferior to (I). Et oleate with H_2 + Cu-Mo oxide affords Et stearate; with H_2 + Cu-V oxide, octadecyl stearate, m.p. 62°, and a little octadecanol result. H. B.

Odorous constituents of Matsutake.—See A., III, 107.

Essential oil of green tea. VIII. Linalool and acetophenone. S. TAKEI, Y. SAKATO, and M. ONO (Bull. Inst. Phys. Chem. Res. Japan, 1937, 16, Abs. 3).—Oxidation of dihydrolinalool (I) gives $\beta\gamma$ -dimethyloctane- $\beta\gamma$ -diol- γ -one (2:4-dinitrophenylhydrazones, m.p. 115—117°; p-nitrophenylhydrazones, m.p. 168°), also obtained from methylheptenone and MgEtI . (I) is therefore $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}\cdot\text{CH}_2\text{Me}$. From green-tea oil, linalool and CPhMe have been isolated. F. R. S.

Preparation of halogenoalkines with the triple linking as far as possible from the halogen atom. Synthesis of dehydroundecylenyl alcohol [Δ^1 -undecinen- λ -ol] and dehydroundecylenyl bromide [λ -bromo- Δ^1 -undecene]. A. OSKERKO (Ber., 1937, 70, [B], 55—61).—Distillation of castor oil at 130—150°/75—100 mm. and passage of the vapours over heated pumice gives homogeneous Δ^1 -undecenoic acid, b.p. 142—145°/2—3 mm., m.p. 24° (yield 10%), transformed into μ -dibromoundecioic acid and thence into Δ^1 -undecenoic acid (I), b.p. 145°/15 mm., m.p. 42°. (I) is readily esterified to Et, b.p. 117°/3 mm. (compound, $\text{C}_{13}\text{H}_{21}\text{O}_2\text{Ag}, \text{AgNO}_3$), and Me Δ^1 -undecenoate. The esters are reduced by Na and EtOH (BuOH) to Δ^1 -undecinen- λ -ol

(II), b.p. 108—109°/2 mm., f.p. -4° (compound, $\text{C}_6\text{H}_5\text{C}(\text{OCH}_2)_3\text{CH}_2\text{OH}\cdot\text{AgNO}_3$; *phenylurethane*, m.p. 51° ; *acetate*), complete absence of moisture appearing essential to success. (II) is converted by PBr_3 in Et_2O containing a little $\text{C}_6\text{H}_5\text{N}$ into λ -*bromo- Δ^a -undecine*, b.p. 98—99°/2 mm., which gives an unstable compound with AgNO_3 . $\text{C}_6\text{H}_5\text{N}$ by itself appears to lead to undesired by-products. H. W.

Metal alkoxides and ortho-esters. II. Thermal decomposition of metal alkoxides and ortho-esters. H. MEERWEIN and E. GESCHKE (J. pr. Chem., 1936, [ii], 147, 203—210; cf. A., 1930, 59).— $\text{Sn}(\text{OEt})_4$ when heated (sealed vessel; 125—170°; 2—10 hr.) in $\text{EtOH}\text{--}\text{N}_2$ (or alone) gives $\text{Sn}(\text{OEt})_2$, MeCHO , and EtOH : crystals of the substance $[\text{Sn}^{\text{IV}}(\text{OEt})_6]\text{Sn}^{\text{II}}$ separate. Above 150° further condensation of MeCHO occurs. $[\text{Sn}(\text{OEt})_6]\text{H}_2$ and $[\text{Sn}(\text{OEt})_6]\text{HNa}$ (I) (*loc. cit.*) decompose similarly but more rapidly owing to the accumulation of OEt on Sn . The Ca , Al , and Zn salts corresponding with (I) do not decompose so rapidly as (I), as they are split in EtOH into their components. The ethoxides of Fe^{III} and Sb^{V} readily decompose giving MeCHO and a lower ethoxide of the metal, the former also giving a black cryst. compound and the latter some $\text{CHMe}(\text{OEt})_2$. The ethoxides of Cu , Co , Ni , and Te^{IV} decompose to MeCHO , EtOH , and the metal, whilst those of Al , Si , Sb^{III} , and Sn^{II} do not decompose under the above conditions but do so differently at higher temp. The yield of aldehyde from $\text{Te}(\text{OEt})_4$ and $\text{Te}(\text{OMe})_4$ is unexpectedly small. H. G. M.

Reducing action of metal alkoxides. II. H. MEERWEIN [with B. VON BOCK, B. KIRSCHNICK, W. LENZ, and A. MIGGE] (J. pr. Chem., 1936, [ii], 147, 211—225; cf. A., 1925, i, 1239).—The following alcohols have been obtained in good yield by reduction of the corresponding aldehyde or ketone with an alkoxide of Al or Mg : β -chloro-, b.p. 159° , and β -bromo-, b.p. $69\text{--}70^{\circ}/13$ mm., -crotonyl; β -chloro-, m.p. 14° , b.p. $147\text{--}149^{\circ}/17$ mm., and β -bromo-, m.p. 18° , b.p. $151\text{--}153^{\circ}/13$ mm., -cinnamyl; o-, m.p. $60\text{--}5\text{--}61^{\circ}$, m., m.p. $51\text{--}51\cdot5^{\circ}$, and p-, m.p. $127\cdot5\text{--}128^{\circ}$, -nitro-cinnamyl; $\alpha\alpha\gamma\gamma$ -, b.p. $87\text{--}89^{\circ}/14$ mm., and $\alpha\gamma\gamma\gamma$ -, b.p. $80\text{--}90^{\circ}/14$ mm., -tetrachloropropan- β -ol; *hydroxycitronellol* ($\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$), b.p. $140\text{--}141^{\circ}/4\text{--}5$ mm. Details for the reduction of crotonaldehyde to the alcohol are given, but the formation of $\text{Bu}^{\text{a}}\text{OH}$ has not been confirmed (cf. A., 1934, 176). Phenolic aldehydes may also be reduced if previously methylated. Reduction of $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is difficult probably owing to complex formation between NMe_2 and the Al alkoxide. The yield of β -butylene glycol from aldol and $\text{Al}(\text{OEt})_3$ is poor. Reduction of COPh_2 by $\text{Al}(\text{OEt})_3$ is different from the foregoing reductions; some CH_2Ph_2 and AcOH are formed, and these are also obtained from $\text{Al}(\text{OEt})_3$ and $\text{CHPh}_2\cdot\text{OH}$, but not $(\text{CHPh}_2)_2\text{O}$. The yields of the various products obtained by reduction of PhCHO by the ethoxides of Al , Zr , Sn^{IV} , Sn^{II} , Sb^{V} , Sb^{III} , Te , Ti , and Fe^{III} are recorded. Excellent yields of $\text{CH}_2\text{Ph}\cdot\text{OH}$ are obtained by means of the first three ethoxides only, and no reduction at all occurs with the ortho-esters of B , As , P , and Si . The mechanism is considered to involve the formation of an additive

complex between the ethoxide and the aldehyde (or ketone) (cf. A., 1930, 59). H then migrates from the alcoholic to the aldehydic constituent of the complex, which immediately decomposes:

$$\text{R}\cdot\text{CHO}\cdots\text{Al}(\text{O}\cdot\text{CH}_2\cdot\text{R}')_3 \rightarrow \text{R}\cdot\text{CH}_2\cdot\text{O}\cdot\text{Al}(\text{O}\cdot\text{CH}_2\cdot\text{R}')_2 + \text{R}'\cdot\text{CHO}$$

(cf. preceding abstract). $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ when heated with the benzyloxides of Al , Mg , Zn , and Ca in $\text{CH}_2\text{Ph}\cdot\text{OH}$ gives $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$ (I), PhCHO , and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{CH}_2\text{Ph}$ (II). The yields of (I) and (II) depend on the benzyloxide used, that of (I) diminishing and that of the ester (II) increasing with the benzyloxides in the foregoing order. The relation between the mechanisms for reduction and ester formation is discussed. The results support the view that ester formation is diminished in favour of reduction with decreasing electropositive character of the metal atom (*i.e.*, increasing homopolar character of the alkoxide). H. G. M.

Reduction products of disaccharides; maltitol, lactitol, cellobiitol. P. KARRER and J. BÜCHI (Helv. Chim. Acta, 1937, 20, 86—90).—Hydrogenation (Ni) of maltose in aq. MeOH at $130\text{--}140^{\circ}/30$ atm. yields maltitol (I), $\text{C}_{12}\text{H}_{24}\text{O}_{11}$, a colourless, hygroscopic powder, $[\alpha]_D$ about $+90^{\circ}$ in H_2O (non-acetate, m.p. about 86°). Lactitol (II), $[\alpha]_D$ about $+14\cdot84^{\circ}$ in H_2O , and cellobiitol (III), $[\alpha]_D$ $-8\cdot8^{\circ}$ in H_2O , are obtained similarly from lactose and cellobiose. The compounds are indifferent towards Fehling's solution and are hydrolysed by acids to 1 mol. of sugar and 1 mol. of sorbitol (tribenzylidenesorbitol, m.p. $190\text{--}191^{\circ}$). (I) is hydrolysed by yeast extracts and by the snail enzyme (IV). (II) and (III) are so slowly attacked by emulsin that hydrolysis appears doubtful, whereas they are readily saccharified by (IV). H. W.

Formation of ethers by the interaction of primary alcohols and olefines at high pressures.—See A., I, 134.

Catalytic hydrolysis of [ethyl] ether.—See A., I, 144.

Action of phosphoric oxide on ether. T. WAGNER-JAUREGG and H. GRIESSHABER (Ber., 1937, 70, [B], 1—8).—Cautious hydrolysis of the "Et metaphosphate" (I) of Langheld obtained from Et_2O and P_2O_5 in CHCl_3 (A., 1910, i, 536; 1911, i, 705; 1912, i, 156; also Wertyporoch *et al.*, A., 1934, 392) shows that only 20—25% of the total phosphate is readily eliminated. Fractional pptn. of the corresponding Ba salts by EtOH from dil. AcOH affords an OEt -richer portion from which PO_4 is obtained with difficulty and a material containing little OEt and readily hydrolysed. This fraction yields *brucine metaphosphate*, $4\text{HPO}_3\cdot 3\text{C}_{22}\text{H}_{26}\text{O}_4\text{N}_2\cdot 16\text{H}_2\text{O}$, (anhyd.) m.p. $188\text{--}190^{\circ}$ (corr.) in sealed capillary. [A similar abnormal composition is shown by *acridinium metaphosphate*, $4\text{HPO}_3\cdot 3\text{C}_{13}\text{H}_9\text{N}\cdot 4\text{H}_2\text{O}$, m.p. $275\text{--}278^{\circ}$ (corr.), and is ascribed to the presence of 3 primary OH in the tetrameride $\text{PO}_2\cdot\text{O}\cdot\text{PO}(\text{OH})\cdot\text{O}\cdot\text{PO}(\text{OH})\cdot\text{O}\cdot\text{PO}(\text{OH})_2$; acridine pyrophosphate is $2\text{H}_4\text{P}_2\text{O}_7\cdot 3\text{C}_{13}\text{H}_9\text{N}$, whereas the corresponding orthophosphate, m.p. $293\text{--}294^{\circ}$ (corr.), is $\text{C}_{13}\text{H}_9\text{N}\cdot\text{H}_3\text{PO}_4$.] The unfractionated solution of (I) gives with brucine in $\text{EtOH}\text{--}\text{H}_2\text{O}$ the normal salt, $\text{EtH}_2\text{PO}_4\cdot 2\text{C}_{22}\text{H}_{26}\text{O}_4\text{N}_2$, m.p. 160° after marked soften-

ing at 140°, decomp. 185—190°, transformed by crystallisation from COMe_2 into the *H* salt, $\text{EtH}_2\text{PO}_4 \cdot \text{C}_{22}\text{H}_{26}\text{O}_4\text{N}_2 \cdot 4\text{H}_2\text{O}$, m.p. 211—214° (corr.), also obtained from Na_2EtPO_4 and brucine hydrochloride. It appears therefore that Et_2HPO_4 is formed in very small proportion if at all by addition of H_2O to (I). The hydrolysate contains EtH_2PO_4 and HPO_3 in agreement with Langheld's conception. Ph_2O and P_2O_5 do not appear to react in CHCl_3 . $(\text{CH}_2\text{Ph})_2\text{O}$ and P_2O_5 in CHCl_3 yield material containing P in very small amount; after its removal a non-homogeneous polymerisate (II) remains from which after treatment with Al_2O_3 in C_6H_6 a mixture of polymeric hydrocarbons is isolated. Dry distillation of (II) gives a yellowish-red oil from which $p\text{-C}_6\text{H}_4\text{Ph}_2$ is isolated in small amount. H. W.

Ethers of Δ^7 -butinen- α -ol. P. A. McCUSKER and J. W. KROEGER (J. Amer. Chem. Soc., 1937, 59, 213—214).— $\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{OR}$ are obtained in 60—75% yield from $\text{OR} \cdot \text{CH}_2\text{CH}_2\text{Br}$ and CH_3CNa in liquid NH_3 ; the following are described: δ -methoxy-, b.p. 87.5°/748 mm., δ -ethoxy-, b.p. 104°/747 mm., δ -butoxy-, b.p. 147—148°/747 mm., and δ - β -bromoethoxy-, b.p. 99—100°/35 mm., Δ^7 -butinene (*Hg* salts, m.p. 113.9°, 98.6—99°, 42.2—42.5°, and 85—86°, respectively); δ - β' -ethoxyethoxy- Δ^7 -butinene, b.p. 84.5—85.5°/34 mm.; di- Δ^7 -butinenyl ether, b.p. 164—165°/750 mm. $\beta\beta'$ -Dibromodiethyl, b.p. 115°/32 mm., and β -bromoethyl β -ethoxyethyl, b.p. 100—101°/33 mm., ethers are prepared from the appropriate OH-ether and PBr_3 in $\text{C}_6\text{H}_5\text{N}$. H. B.

Carbohydrates and polysaccharides. LII. Preparation, separation, and identification of the isomeric propylidene-, isobutylidene-, tert.-amylidene-, and dibromoethylidene-glycerols, and general properties of glycerol cyclic acetals. S. M. TRISTER and H. HIBBERT (Canad. J. Res., 1936, 14, B, 415—426).—Condensation of EtCHO , Pr^iCHO , Bu^iCHO , and $\text{CH}_2\text{Br} \cdot \text{CHO}$ with glycerol at 90° in presence of 40% H_2SO_4 gave in each case a mixture of the 5- and 6-membered cyclic acetals. These were separated as benzoates by means of ligroin, and identified by hydrolysis, followed by methylation and hydrolysis to the glycerol Me_1 ether. In this way EtCHO gave $\alpha\beta$ -, b.p. 70—72°/3 mm. (γ -benzoate, b.p. 147—149°/1 mm.; γ -Me ether, b.p. 67—69°/17 mm.), and $\alpha\gamma$ -propylideneglycerol, b.p. 50—51°/2 mm. (β -benzoate, m.p. 74—75°; β -Me ether, b.p. 89—90°/23 mm.). Pr^iCHO gave $\alpha\beta$ -, b.p. 69—72°/2 mm. (γ -benzoate, b.p. 159—162°/5 mm.; γ -Me ether, b.p. 70—71°/15 mm.), and $\alpha\gamma$ -isobutylideneglycerol, b.p. 55—56°/2 mm. (β -benzoate, m.p. 73.5° β -Me ether, b.p. 80—81°/15 mm.). Bu^iCHO gave $\alpha\beta$ -, b.p. 83—84°/6 mm. (γ -benzoate, b.p. 169°/8 mm.; γ -Me ether, b.p. 66—68°/6 mm.), and $\alpha\gamma$ -tert.-amylideneglycerol, m.p. 45° (β -benzoate, m.p. 93.5°; β -Me ether, b.p. 79—81°/6 mm.). $\text{CH}_2\text{Br} \cdot \text{CHO}$ gave $\alpha\beta$ -, b.p. 124—127°/3 mm. (γ -benzoate, b.p. 167—171°/3 mm.), and $\alpha\gamma$ -(dibromoethylidene)glycerol, b.p. 117—119°/3 mm. (β -benzoate, m.p. 67.5°); the structures of the last two benzoates were proved by direct synthesis from glyceryl α -benzoate.

Increase in the electronegative character of the aldehyde increased the ratio of 5- to 6-membered

cyclic acetal produced, the ratio from Bu^iCHO being 3:2, from Pr^iCHO 3:1, from EtCHO 4:1, and from $\text{CH}_2\text{Br} \cdot \text{CHO}$ 15:1; Bu^iCHO unites with glycerol in absence of a catalyst. High temp. also increases the proportion of 5-membered isomeride. A. LI.

[Catalytic] synthesis of esters by dehydrogenation of alcohols.—See A., I, 143.

Electrolysis of mixtures of propionates with sulphates and with perchlorates. F. FICHTER and P. SUTTER (Helv. Chim. Acta, 1937, 20, 156—158).—The reactions do not yield alkyl and glycol esters (cf. A., 1935, 472). E. S. H.

Cyclisation of geranic acid. K. BERNHAUER and R. FORSTER (J. pr. Chem., 1936, [ii], 147, 199—202).—Geranic acid, best prepared (70% yield) by oxidation of citral with $\text{Ag}_2\text{O} \cdot \text{NaOH} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, is cyclised in good yield (70—80%; cf. lit.) by refluxing (water-bath; 6 hr.) with HCO_2H or with $\text{AcOH} \cdot \text{H}_2\text{SO}_4$, which acids give yields > those obtained with other acids. H. G. M.

Fatty acids. I. Purification of linoleic acid by crystallisation methods. J. B. BROWN and G. G. STONER. II. Preparation of pure oleic acid by a simplified method. J. B. BROWN and G. Y. SHINOWARA (J. Amer. Chem. Soc., 1937, 59, 3—6, 6—8).—I. The acids from cotton-seed and maize oils are separated into saturated and unsaturated (A) by crystallisation from COMe_2 at -20° . Linoleic acid (80—93% pure) is isolable from (A) by fractional crystallisation from COMe_2 or MeOH at -65° to -45° , or by fractionation of the Li salts (from BuOH) or K salts (from EtOH) at -20° to 0° . Details are given.

II. Oleic acid, m.p. 13° , is isolated from the acids from olive oil by fractional crystallisation from COMe_2 at -60° to -20° . H. B.

Highly unsaturated C_{18} -fatty acids in Hokke oil.—See A., III, 55.

Replacement of the hydroxyl group of ethyl (+)lactate by halogens and the molecular dissymmetry of derivatives of ethyl lactate which contain the sulphin group. W. GERARD, J. KENYON, and H. PHILLIPS (J.C.S., 1937, 153—158).—Et (–)lactate (I) with PCl_5 (or PBr_5) in presence of K_2CO_3 or *tert.* bases yields Et (+) α -chloro- [or (+) α -bromo]-propionate. Et (+)lactate (II) and $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{SOCl}_2$ in $\text{C}_6\text{H}_5\text{N}$ afford Et (+) α -*p*-toluenesulphinoxypropionate (III), b.p. $110^\circ/0.1$ mm., $[\alpha]_{\text{D}}^{20} +12.41^\circ$, which can be separated by distillation into fractions of similar composition but widely different rotations. (III) with Cl_2 in H_2O yields Et (–) α -chloropropionate (IV), with Br in CHCl_3 , Et (–) α -bromopropionate, and with HOCl , a mixture of (IV) and (I). Et (–) α -*p*-toluenesulphinoxypropionate, $[\alpha]_{\text{D}}^{20} -21.5^\circ$, with KSCN in EtOH affords Et (–) α -thiocyanopropionate, b.p. $119^\circ/20$ mm., $[\alpha]_{\text{D}}^{20} -7.51^\circ$, and with KSeCN in EtOH , ethyl (–) α -selenocyanopropionate, b.p. $63\text{--}64^\circ/0.1$ mm., $[\alpha]_{\text{D}}^{20} -0.85^\circ$. (II) with SOCl_2 in presence of *tert.* bases yields (IV); in absence of bases, Et (+) α -chlorosulphinoxypropionate, which decomposes on distillation to (IV), with $\text{C}_6\text{H}_5\text{N}$ in Et_2O affords (I) and *N*-chloropyridinium *N*- α -carbethoxyethylsulphinat (picrate, m.p. 95°),

and with H_2O yields (II). *n*-Amyl chlorosulphinate and (I) in $\text{C}_5\text{H}_5\text{N}$ -ligroin afford α -carbethoxyethyl-*n*-amyl sulphite, b.p. $140\text{--}142^\circ/13\text{ mm.}$, $[\alpha]_{\text{D}}^{20} -37.15^\circ$, also prepared from Et $(-)\alpha$ -chlorosulphinoxypionate and *n*- $\text{C}_5\text{H}_{11}\text{OH}$ with $\text{C}_5\text{H}_5\text{N}$ in Et_2O . *n*-Amyl sulphite, b.p. 129.5° , is obtained from SOCl_2 and *n*- $\text{C}_5\text{H}_{11}\text{OH}$, whilst $(+)\alpha$ -carbethoxyethyl sulphite, b.p. $111\text{--}112^\circ/0.1\text{ mm.}$, $161^\circ/14\text{ mm.}$, $[\alpha]_{\text{D}}^{20} +49.60^\circ$, results from SOCl_2 and (II). It is deduced that the *l*-Et esters of lactic, α -chloro- and α -bromo-propionic acids, and the *d*-Et esters of α -thio- and α -selenocyanopropionic acids all have the same relative structure, and that the replacement of OH in Et lactate by Cl or Br, by means of PCl_5 , PBr_5 , or SOCl_2 , either in presence or absence of a *tert.* base, results in a change of configuration. J. D. R.

Chlorohydroxybehenic and glycidic acids from erucic and brassidic acids. K. HASHI (J. Soc. Chem. Ind. Japan, 1936, 39, 469—470B).—Brassidic acid and HOCl give the pure γ -form of chlorohydroxybehenic acid (I), m.p. $62.5\text{--}63.5^\circ$, converted by KOH into glycidobrassicidic acid (II), m.p. $67.3\text{--}68.3^\circ$, which with HCl gives (I). Erucic acid and glycidoerucic acid (III), m.p. $62.3\text{--}63^\circ$, give, under similar conditions, a mixture of the α -form of (I) and a so-called β -form, m.p. $51.5\text{--}52^\circ$ [$58.3\text{--}64^\circ$ when prepared from (III)], believed to be a mixture. Mixtures of (II) and (III) have depressed m.p. and (III) is more sol. than (II) in ligroin and COMe_2 ; (II) and (III) are thus *trans*- and *cis*-forms respectively. R. F. P.

Action of hydrazine hydrate on lactones. A. DARAPSKY, H. BERGER, and A. NEUHAUS (J. pr. Chem., 1936, [ii], 147, 145—160).— γ -Valerolactone with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -EtOH (water-bath; 8 hr.) gives γ -hydroxy-*n*-valerhydrazide, m.p. 65° (CHPh derivative, m.p. 95°), described by Blaise *et al.* (A., 1905, i, 329) as a hydrazinolactone, m.p. $61\text{--}62^\circ$. It is not converted by HNO_2 into the expected azide. *o*-Hydroxydiphenylacetylhydrazide, prepared similarly from the appropriate lactone (I), and reconverted into it by HCl or warm $\text{AcOH}\text{--}\text{H}_2\text{O}$, gives with HNO_2 the azide (II), which decomposes in boiling C_6H_6 to (I), with $\text{NH}_2\text{Ph}\text{--}\text{C}_6\text{H}_5$ yields the corresponding anilide, m.p. 175° (lit. $143\text{--}146^\circ$), and with hot EtOH gives (I) and a mixture which contains the expected urethane and on hydrolysis gives some *o*-hydroxybenzhydramine. On keeping (II) decomposes to the compound, $\text{CHPh}\langle\text{C}_6\text{H}_4\text{--NH--CO}\rangle\text{O}$, m.p. 219° (*o*-hydroxybenzhydramine carbamic anhydride), hydrolysed by HCl to *o*-hydroxybenzhydramine and cyclo-*o*-phenylenebenzylidene oxide (A., 1895, i, 537), the latter being the sole isolable product of hydrolysis with NaOH. Coumarin (III) with hot $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -EtOH yields β -hydrazino-*o*-hydrocoumarinhydrazide (IV), m.p. $128\text{--}129^\circ$ [$(\text{CHPh})_2$ derivative, m.p. 141°], which on prolonged contact with EtOH and on hydrolysis with HCl gives (III). The constitution of (IV) is confirmed by its conversion by HNO_2 into 1-nitroso-5-*o*-hydroxyphenyl-5-pyrazolidone, m.p. 126° [NH_4 , m.p. 132° (decomp.), and Ag salt], which closely resembles the known, corresponding 5-Ph compound and with Br- AcOH gives 4:4-dibromo-3-*o*-hydroxyphenyl-5-pyrazolone, m.p. 178° , which is readily sol. in dil. NaOH. Et *o*-hydroxy-

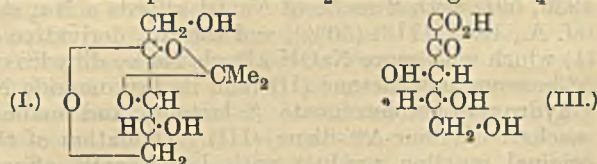
benzoylacetate could not be obtained from Et salicylate, EtOAc, and Na. H. G. M.

Investigation of oxalic acid dihydrate by Fourier analysis from X-ray crystal data.—See A., I, 68.

Reaction of monosubstituted malonic esters and methylenedimalonic esters with sodium ethoxide. J. R. ROLAND and S. M. McELVAIN (J. Amer. Chem. Soc., 1937, 59, 132—135; cf. A., 1935, 961, 1224).—The predominant reaction occurring when $\text{CHMe}(\text{CO}_2\text{Et})_2$ (I) (1 mol.) is heated with NaOEt (0.5 mol.) at 160° (not at $50\text{--}60^\circ$ or $100\text{--}120^\circ$) is ethylation of the Na enolate of (I) by (I): $\text{CHMe}(\text{CO}_2\text{Et})_2 + [\text{CMe}(\text{CO}_2\text{Et})_2]\text{Na} \rightarrow \text{CMeEt}(\text{CO}_2\text{Et})_2$ (II) + $\text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na}$ (III). (II), (III) (as acid), Et α -methylbutyrate [formed from (II)], and some Et CO_2Et are isolated. No intermol. condensation occurs. Similarly, $\text{CHPr}^i(\text{CO}_2\text{Et})_2$ and NaOEt at $150\text{--}160^\circ$ give Et isovalerate, Et α -isopropylbutyrate, and $\text{CPr}^i\text{Pr}^i(\text{CO}_2\text{Et})_2$. (I) could not be condensed with $\text{Pr}^i\text{CO}_2\text{Et}$. Et propane- $\alpha\gamma\gamma$ - and heptane- $\alpha\alpha\eta\eta$ -tetracarboxylates do not undergo intramol. condensation with NaOEt at $110\text{--}130^\circ$; products resulting from decarboxylation and retrograde Michael reactions are isolable. Et dodecane- $\alpha\mu\mu$ -tetracarboxylate similarly affords a viscous intermol. condensation product. H. B.

Synthesis of $\alpha\alpha'$ -diethoxy straight-chain acids. M. MEYER (Compt. rend., 1936, 203, 1370—1372; cf. A., 1936, 1231).—Et $_2$ sodioethoxymalonate in boiling PhMe-EtOH with $\text{CH}_2(\text{CH}_2\text{Br})_2$, affords Et $_4$ $\alpha\alpha'$ -diethoxypentane- $\alpha\alpha\alpha'$ -tetracarboxylate (I), b.p. $130\text{--}131^\circ/3\text{ mm.}$, and Et $_2$ ethoxy- γ -bromopropylmalonate, b.p. $170\text{--}171^\circ/3\text{ mm.}$ Similarly, $(\text{CH}_2\text{Br}\cdot\text{CH}_2)_2$ and $\alpha\eta$ -dibromodecane afford Et $_4$ $\alpha\zeta$ -diethoxyhexane- $\alpha\alpha\zeta$ -tetracarboxylate (II), b.p. $129^\circ/2.5\text{ mm.}$, Et $_2$ ethoxy- δ -bromobutylmalonate, b.p. $174\text{--}175^\circ/3\text{ mm.}$, Et $_4$ $\alpha\mu$ -diethoxydodecane- $\alpha\mu\mu$ -tetracarboxylate (III), b.p. $185^\circ/2\text{ mm.}$, and Et $_2$ ethoxy- μ -bromodecylmalonate, b.p. $222^\circ/2\text{ mm.}$, respectively. (I), (II), and (III) with aq. EtOH-KOH afford the corresponding tetracarboxylic acids, m.p. $190\text{--}191^\circ$, $218\text{--}220^\circ$ (block) ($+4\text{H}_2\text{O}$, decomp. 178°), $110\text{--}112^\circ$ (decomp.), respectively, decarboxylated to give diastereoisomerides of $\alpha\alpha'$ -diethoxy-pimelic, m.p. 115° and 82° , -suberic, m.p. 113° and $79\text{--}81^\circ$, and -dodecamethylenedicarboxylic acid, m.p. 85° and 69.5° , respectively. J. L. D.

Synthesis of *d*-xylosonic acid. R. PRINCE and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 101—109).—Hexosonic acids are very much more stable than pentosonic acids; it is very doubtful if the unknown tetrosomic acids are capable of existence. *d*-Arabinose is hydrogenated (Ni) to *d*-arabitol, which is transformed by oxidative fermentation into *d*-xyloketose. This passes in COMe_2 containing CuSO_4 and



H_2SO_4 at room temp. into 2:3-isopropylidene-*d*-xyloketose (I), needles, m.p. $67\text{--}68^\circ$, and (?) an

isomeride, rhombohedra, m.p. 81.5–83°, $[\alpha]_D^{18}$ 0° ± 1° in COMe₂. (I) is oxidised by KMnO₄ in alkaline solution to *K* 2 : 3-isopropylidene-*d*-xylosonate (+0.5H₂O), m.p. 264–265° (corr.; decomp.), whence 2 : 3-isopropylidene-*d*-xylosonic acid (II), m.p. 174–175° (corr.), $[\alpha]_D^{18}$ –12° in COMe₂. Hydrolysis of (II) to *d*-xylosonic acid (III) without isomerisation of the latter to *d*-erythroascorbic acid is best effected by approx. 2*N*-mineral acid at 20°, whereby syrups are produced which reduce Fehling's solution but are not immediately active towards I in acid solution; activity is readily acquired by long keeping or short warming in H₂O or EtOH.

H. W.

Oxidation of ascorbic acid and its reduction *in vitro* and *in vivo*. H. BORSOOK, H. W. DAVENPORT, C. E. P. JEFFREYS, and R. C. WARNER (J. Biol. Chem., 1937, 117, 237–279; cf. Herbert *et al.*, A., 1933, 1143).—Reversible oxidation of ascorbic acid (I) gives first dehydroascorbic acid (II) which, in H₂O at room temp. and $p_H < 4$, undergoes spontaneous irreversible change, yielding an acid (III) (possibly $\alpha\beta$ -diketo-*l*-gulonic acid) stronger than (II), having greater reducing power, not reduced by H₂S in acid solution or by glutathione (IV) in neutral or alkaline solution, and non-antiscorbutic. This change is independent of the presence of air or oxidising agents. (III) undergoes reversible oxidation yielding *l*-threonic (V) and oxalic acids possibly by way of another intermediate. There is also a third oxidation stage which is rapid at neutrality and alkaline reaction, (V) being possibly the substance which is then oxidised. The oxidation-reduction potentials of the three stages of oxidation have been determined and the first acid dissociation consts. of (II) and (III) have been measured. The oxidation (I) \rightleftharpoons (II) is the only one which is physiologically reversible and significant for antiscorbutic action. (I) is very slowly oxidised in human whole blood and remains much longer reduced in whole blood than in plasma. Human blood does not reduce (II) or retard its conversion into (III). Erythrocytes (man, ox, cat, dog, pig, rat, sheep) are impermeable or almost so to (I). (I) and (II) have the same antiscorbutic potency, but *in vitro* at the p_H and temp. of the tissues (II) is rapidly and irreversibly inactivated. In the tissues (II) is rapidly reduced, and hence retains its potency, the chief reducing agent being probably (III). Conditions affecting the reaction between (II) and (III) are described.

W. McC.

Autoxidation of ascorbic acid and its inhibition by sulphur compounds.—See A., III, 104.

Decomposition of double lactones of *d*-mannose sugar acids with alkali and with alkaline iodine. K. REHORST (Naturwiss., 1937, 25, 13–14; cf. A., 1926, 51).—*d*-Mannosaccharodilactone (I) (A., 1936, 591) with 2 mols. of NaOH affords a Na₂ salt (cf. A., 1932, 1113) (50%), and the Na₁ derivative of (I) which with more NaOH affords Na $\alpha\gamma$ -dihydroxy- Δ^7 -hexenoate β -lactone (II) (and its tautomeride Na α -hydroxy- γ -ketohexenoate β -lactone) and mannosaccharodilactone- $\Delta^{\alpha\alpha}$ -diene (III). Oxidation of the original reaction product with I in NaOH affords H₂C₂O₄ and CHI₃ from (II) quantitatively. The total unsaturation less that due to (II) gives (III). J. L. D.

$\alpha\alpha$ -Disulphodipropionic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1937, 12, A, No. 13, 17 pp.).—*meso*- $\alpha\alpha$ -Disulphodipropionic acid (I), m.p. 118–119° (*brucine*, +6H₂O and anhyd., and *strychnine*, +5H₂O and anhyd., salts), is isolated as its β -*naphthylamine* salt (not pure) from the eutectic mixture, m.p. 105°, of the *dl*- (II) (32%) and *meso*-acid which remains after crystallisation of (II) in the prep. from K₂S₂ and CHMeBr·CO₂H. Resolution of (II) with *brucine* to give the *d*-acid (III) (*brucine* salt, +6.5H₂O and anhyd.) is described. The solubility of (I), (II), or (III) in H₂O at 25° remains const. for long periods (200 hr.) and then increases only slowly due to slight decomp., showing that no interconversion (I) \rightleftharpoons (II) occurs. In alkaline solution polarimetric measurements show that a rapid reciprocal oxidation-reduction occurs between *dl*-SH·CHMe·CO₂H and (III) and, under these conditions, the equilibrium (I) \rightleftharpoons (II) is established. The oxidation-reduction occurs only slowly in acid solution and the results are not reproducible. The vals. $K_1 \times 10^4$ 7.3 and 7.0 are obtained for (I) and (II), respectively, by conductivity measurements.

J. W. B.

Ethylcarolic acid, C₁₁H₁₄O₄, m.p. 89°, from *Penicillium terrestre*, Jensen; also *l*-hexolactone, b.p. 219°.—See A., III, 71.

Influence of carriers on catalysts.—See A., I, 143.

Analysis of γ -fructoside mixtures by means of invertase. V. METHYLATED and acetylated derivatives of crystalline α -methyl- and α -benzylfructofuranoside. C. B. PURVES and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 49–56).—The cryst. γ -methylfructoside (of A., 1934, 413) is now shown to be α -methylfructofuranoside (I), new m.p. 80.5–81°, $[\alpha]_D^{20}$ +93° in H₂O. When (I) is treated with Et₂O·TiOEt in EtOH and the solvents removed in a vac. at \approx room temp. a Ti₂ derivative is obtained; this with MeI in Et₂O gives a liquid *dimethyl- α -methylfructofuranoside* (II), $[\alpha]_D^{20}$ +94° in CHCl₃, hydrolysed (0.1*N*-HCl at 100°) to a liquid (? 3 : 4) *dimethylfructose*, $[\alpha]_D^{20}$ (in H₂O) –10.9° \rightarrow –17.2°. (II) is methylated further (as above) to the liquid *tetramethyl- α -methylfructofuranoside*, $[\alpha]_D^{20}$ +115.9° in CHCl₃, hydrolysed to *tetramethylfructofuranose* (III). Crude (I) (prep. from sucrose; A., 1934, 1207) is acetylated (Ac₂O, NaOAc) to *α -methylfructofuranoside tetra-acetate*, m.p. 48–48.5°, $[\alpha]_D^{19}$ +88.1° in CHCl₃. (I) and HCl (1 mol.) in dioxan give an unstable additive compound which decomposes rapidly; the reaction is studied (in dil. solution) polarimetrically and by the Cu-reducing power. The data indicate the formation of unstable reducing Cl-compounds which undergo some change prior to further reaction with the solvent; the behaviour of (I) and sucrose with MeOH-HCl (*loc. cit.*) is thus explicable. (I) and CH₂Ph·OH-HCl give a reducing substance (IV), an invertase-hydrolysable benzyl derivative (V), and *α -benzylfructofuranoside* (VI), m.p. 89°, $[\alpha]_D^{20}$ +45.7° in H₂O, purified through its *tetra-acetate*, m.p. 84.5–85°, $[\alpha]_D^{20}$ +64.7° in CHCl₃; (IV) and (V) are removed from the mixture by fermentation. (VI) is hydrolysed (0.25*N*-HCl at 20°) 16.5 times as fast as sucrose. Methylation (TiOEt method) affords a liquid *Me₂* derivative, $[\alpha]_D^{19}$ +57.1°

in dioxan, further methylated to the liquid *Me*₂ derivative, $[\alpha]_D^{20} + 83.3^\circ$ in CHCl_3 , which with MeOH-HCl followed by aq. HCl gives (III). (VI) is partly converted into a CH_2Ph derivative, $[\alpha]_D^{20}$ (calc.) $-27 \pm 2^\circ$ in H_2O , by $\text{CH}_2\text{Ph}\cdot\text{OH-HCl}$. H. B.

Anthraquinone colouring matters: galiosin; rubiadin primveroside. R. HILL and D. RICHTER (J.C.S., 1936, 1714—1719).—Galiosin (I) is obtained from fresh madder root by BuOH and shown to be *purpurin-3-carboxylic acid-1- β -primveroside*, $+6\text{H}_2\text{O}$. *Galium verum* roots yield *rubiadin-3- β -primveroside* (II), m.p. $248-250^\circ$ (red *Ba* and *Pb* salts), the structure of which is proved by hydrolysis to *d*(+)-xylose and *rubiadin-3-glucoside*. (I) is hydrolysed by cold dil. acid or alkali or in a few hr. by hot H_2O to *purpurin-3-carboxylic acid* (III) (absorption bands in PhMe , NaOH , and $\text{H}_2\text{SO}_4\text{-H}_3\text{BO}_3$ detailed), also isolated from *G. verum*, *G. Mollugo*, and commercial (not fresh) madder and synthesised by condensation of CH_2O and *purpurin* in H_2SO_4 to *3-hydroxymethyl-purpurin*, m.p. $>300^\circ$ (*Na* salt), which is oxidised to (III) by $\text{NaNO}_2\text{-H}_2\text{SO}_4\text{-H}_3\text{BO}_3$. (I) with very dil. acid gives *primverose*, identified by hydrolysis by $0.5N\text{-H}_2\text{SO}_4$ to glucose and *d*(+)-xylose. The position of the sugar in (I) is determined by its ready hydrolysis, colour reactions, lack of reducing properties, and reduction by $\text{Na}_2\text{S}_2\text{O}_4$ and by H_2 -colloidal Pd to *munjistin*. Both (I) and (II) are hydrolysed by the enzymes of *Primula officinalis* and *vulgaris*.

R. S. C.

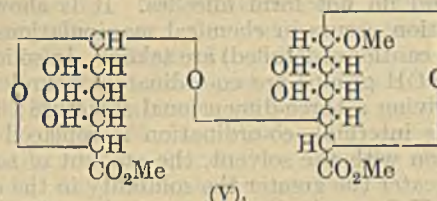
Xylyl- β -*d*-glucoside. T. KITASATO (J. Biochem. Japan, 1936, 24, 327—336).—The rates of hydrolysis of the xylyl- and tolyl- β -glucosides by emulsin (at p_H 5.0 and 30°) give an order (2:3-xylyl- and 2-tolyl- β -*d*-glucoside greatest, respectively) which is exactly the reverse of the order (2:6-xylyl- and 4-tolyl- β -*d*-glucoside greatest, respectively) given by acid hydrolysis (in $0.02N\text{-HCl}$ at room temp.). The following β -*d*-glucosides were prepared ($[\alpha]_D^{20-22}$ in H_2O): 2:3-xylyl-, m.p. $190-191^\circ$, $[\alpha] -65.1^\circ$; 2:5-xylyl-, m.p. 170° , $[\alpha] -68.8^\circ$; 3:5-xylyl-, m.p. $203-204^\circ$, $[\alpha] -67.7^\circ$; 3:4-xylyl-, m.p. $173-174^\circ$, $[\alpha] -66.9^\circ$.

F. O. H.

Glycyrrhizin. I. W. VOSS, P. KLEIN, and H. SAUER. II. Novel disaccharide as sugar component of glycyrrhizin. W. VOSS and J. PEIRSCHKE (Ber., 1937, 70, [B], 122—132, 132—137).—I. Successive crystallisations of "glycyrrhizinium ammoniacale" from AcOH and EtOH followed by extraction of the product with Et_2O gives NH_4H_2 glycyrrhizate (I), $\text{C}_{42}\text{H}_{65}\text{O}_{16}\text{N}$, $[\alpha]_D^{25} + 43.3^\circ$ in H_2O , converted by 1% H_2SO_4 into glycyrrhizic acid (II), $\text{C}_{42}\text{H}_{63}\text{O}_{16}$, $2\text{H}_2\text{O}$, $[\alpha]_D^{20} + 58.5^\circ$ in abs. EtOH (K_3 , $[\alpha]_D^{19} + 44.8^\circ$ in H_2O , and $K\text{H}_2$, $[\alpha]_D^{19} + 43.5^\circ$ in H_2O , salts), the composition of which is most surely deduced from analysis of the salts. (II) is hydrolysed by 1% H_2SO_4 at $150-155^\circ$ to α -glycyrrhetic acid (III), $\text{C}_{30}\text{H}_{46}\text{O}_4$, m.p. 283° , $[\alpha]_D^{20} + 140^\circ$ in abs. EtOH (*Na* salt, m.p. $303-304^\circ$, $[\alpha]_D^{22} + 130^\circ$ in abs. EtOH ; *K* salt, m.p. 293° , $[\alpha]_D^{20} + 92.4^\circ$ in abs. EtOH ; *Ac* derivative, m.p. 308° , $[\alpha]_D^{22} + 122^\circ$ in abs. EtOH ; *Me* ester (IV), m.p. 229° , $[\alpha]_D^{20} + 106^\circ$ in abs. EtOH ; *Et* ester, m.p. 204° , $[\alpha]_D^{21} + 116^\circ$ in abs. EtOH , obtained from (II) and MeOH-HCl or by alcoholysis of (II). (IV) contains 1 OH and does not

react with NH_2OH , HCl or $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, HCl and NaOAc . Treatment of (IV) with $\text{KOH-EtOH-H}_2\text{O}$ at room temp. gives unchanged material and β -glycyrrhetic acid, $\text{C}_{30}\text{H}_{46}\text{O}_4$, m.p. 296° , $[\alpha]_D^{21} + 86^\circ$ in abs. EtOH (*Me* ester, m.p. 251° , $[\alpha]_D^{20} + 90^\circ$ in abs. EtOH ; *Ac* derivative, m.p. 291° , $[\alpha]_D^{20} + 109^\circ$ in abs. EtOH). H. W.

II. Hydrolysis of (II) by 1% aq. H_2SO_4 is accompanied by an unusually ready decomp. of the uronic acids formed, which also occurs when (I) is heated with MeOH-HCl on the water-bath. The best conditions are secured when (II) is treated with MeOH-HCl at $>40^\circ$, whereby a *Me*₂ 1-methyldihexuronate, (V), m.p. 223° , $[\alpha]_D^{19} + 26.5^\circ$ in H_2O , is obtained. It is converted by aq. Ba(OH)_2 at room temp. into the corresponding acid [*brucine* salt, anhyd. and $+5\text{H}_2\text{O}$, m.p. 206° (decomp.) after becoming yellow at 200°], also obtained by use of 2% H_2SO_4 at 80° . The



mother liquors from (V) contain non-cryst. substances hydrolysed by 2% H_2SO_4 at 80° to an acid which gives a *Ba* salt, $\text{C}_{12}\text{H}_{18}\text{O}_{14}\text{Ba}$, $[\alpha]_D^{19} -5.2^\circ$, and a *brucine* salt, anhyd. and $+2.5\text{H}_2\text{O}$, m.p. 182° (decomp.) after darkening at 170° , $[\alpha]_D^{19} -26.9^\circ$ in H_2O .

H. W.

Polysaccharide synthesised by a soil micro-organism. W. Z. HASSID and W. L. CHANDLER (J. Biol. Chem., 1937, 117, 203—207).—A non-spore-bearing bacterium from a mud brick (A.D. 400) from the West Egyptian desert when propagated in a medium containing 0.2% of mannitol as sole org. C source produced a non-reducing, N-free polysaccharide (I), $[\alpha]_D + 140^\circ$ in H_2O (*triacetate*, $[\alpha]_D + 148^\circ$ in CHCl_3 , mol. wt. $2675-2980$), which gave a 96.5% yield of glucose on acid hydrolysis. The I val. of (I) (cf. Bergmann *et al.*, A., 1930, 457) was 2.5. Hence it contained approx. 9—10 anhydroglucose units. W. McC.

Highly polymerised compounds. CL. Constitution of starch. H. STAUDINGER and E. HUSEMANN (Annalen, 1937, 527, 195—236; cf. A., 1936, 710).—In starch solutions the ageing effects, the influence of electrolytes on η , and aberrations from the Hagen-Poiseuille law are due to the P content and are not observed with P-free products. The main reasons for belief in the micellar nature of starch solutions are thus invalid; only the low apparent mol. wts. are still inexplicable on the macro-mol. theory, but this is so also for other polysaccharides. P-free starch is unaffected by dissolution and reprecipitation. The differences between different starches are due to the differing average size of the mol., but no one starch is a chemical individual; all are mixtures of polymers, forming a polymeric-homologous series. If potato-starch is heated with $2N\text{-HCl}$ at 100° for 1.75—3.5 min., cooled for 30 sec. in ice, and poured into MeOH , the ppt. is a starch, the degree of degradation

of which depends on the time of heating. It is freed from P by addition of MeOH to its solution in cold HCO_2H until the ppt. becomes granular; the P-containing amylopectin is first pptd. The final products obtained are not homogeneous, but can be fractionally pptd. The mol. wt. of the variously degraded starches, measured osmotically through an ultracellafilter in $\text{HCO}\cdot\text{NH}_2$, by extrapolation (van 't Hoff's law is not obeyed) are 30,000—153,000; η is measured in $\text{HCO}\cdot\text{NH}_2$ and leads to the same K_m , 0.63×10^{-4} , for all fractions. The triacetates (prep. by careful treatment with $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$), the starches obtained therefrom by NaOMe (rigid absence of O_2), the Me ethers (prep. by Haworth's method; about 1.5 OMe), the Me ether acetates, and the nitrates (about 2.5 NO_2) are shown by the same methods, but in other solvents, to have the same mol. wt. and K_m . This is regarded as final proof that the products are macro-mols. and do not form micelles. It is shown that degradation occurs in chemical manipulations unless rigid precautions (detailed) are taken. In solid starch the free OH groups are co-ordinately bound to each other, giving a three-dimensional structure; in solution this intermol. co-ordination is replaced by co-ordination with the solvent, the amount of solvation being greater the greater the solubility in the solvent. In hot H_2O much disruption of the solid linkings occurs with formation of hydrated mols., which, however, are unstable in cold H_2O ; thus, in aq. solutions gradual decomp. of the hydrate occurs with liberation of OH and consequent formation of OH-OH linkings, leading to pptn. of solid starch. The $\text{HCO}\cdot\text{NH}_2$ solvate is more stable and solutions in $\text{HCO}\cdot\text{NH}_2$ are thus stable. These views do not apply to P-containing starch, which is heteropolar, for, firstly, the lyophilic groups increase the solubility and, secondly, several macro-mols. may be bound by one P. P-free starch is a branched-chain mol., each 2—4 glucose residues of the central chain carrying a side-chain of about 20 glucose units attached glucosidically to the O at 3 or 6. This accounts for Haworth's yields of 2:3:4:6-tetramethylglucose (derived from the terminal unit of each branch) and of 2:6-dimethylglucose (derived from the unit of the centre chain to which the branch is attached), which are thus reconciled with the macro-mol. theory. It accounts also for the fact that cellulose (a straight-chain macro-mol.) has about 10 times as a long a chain (as revealed by K_m) as has starch of the same mol. wt. and consequently has a different colloidal behaviour. The least degraded starch examined contained about 950 glucose units; natural P-free starch has a macro-mol. of >2000 units; P-containing starch is much more complex.

R. S. C.

Hydroxyethyl ethers of cellulose. II. Higher ethers. P. P. SCHORIGIN and J. A. RIMASHEVSKAJA (J. Gen. Chem. Russ., 1936, 6, 1632—1638).—Cellulose dihydroxyethyl ether (I) is prepared by soaking the mono-ether (II) in 33% NaOH, and treating the product with $(\text{CH}_2)_2\text{O}$ in COMe_2 ; the trihydroxyethyl ether (III) is prepared similarly from (I). (II) is sol. in H_2O but not in org. solvents, (I) is sol. in H_2O and EtOH, but not MeOH, and (III) is sol. in H_2O , EtOH, and MeOH; all are insol. in COMe_2 . The η

of the solutions falls in the order (II) $>$ (I) $>$ (III). The ethers are readily acetylated by AcOH in presence of catalysts (H_3PO_4 , ZnCl_2). Various nitrates of the ethers are described.

R. T.

Preparation and properties of dideutero-methylamine. H. J. EMELÉUS and H. V. A. BRISCOE (J.C.S., 1937, 127—130).— $\text{NH}_2\text{Me}\cdot\text{HCl}$ treated with successive quantities of D_2O , followed by liberation of the base with CaO yields dideutero-methylamine, b.p. $-5.2 \pm 0.1^\circ$, m.p. $-89.2 \pm 0.1^\circ$.

J. D. R.

Poly-membered heterocyclic compounds. XI. Preparation of the 14-, 15-, and 17-membered, cyclic imines from aliphatic bromoamines. Survey of the properties of poly-membered, cyclic imines. L. RUZICKA, G. SALOMON, and K. E. MEYER [with M. FURTER and H. GYSEL] (Helv. Chim. Acta, 1937, 20, 109—128).—The requisite bromoalkylamine dissolved in 30 mol.-% EtOH or Pr^iOH is treated with a slight excess of alkali. With increasing concn. the yield of cyclic imine diminishes in favour of the OH-amine, whereas that of polymeric products remains const. The relationship between d and no. of members of cyclic imines and their N -Me derivatives is closely similar to that of carbocyclic compounds, and shows a max. d for a medium no. of C atoms. The mol. refraction of cyclic imines is normal and the m.p. of those solid at room temp. show similar variation and similar abs. vals., as do the cyclic ketones with the same no. of C atoms. The piperidine odour of cyclic imines gradually gives place to that of decay, which is very pronounced with a 9-membered ring. With the 14-membered ring a feeble basic and pronounced musk-like odour are observed. With the 15-membered ring the musk odour is very marked; it reaches a max. with the 16- and 17-rings and is weakened in the 18-ring. N -Me and double linking have little effect on the odour, which appears to be governed by the no. of C in the ring, one or two hetero-members of which merely cause a modification. $[\text{CH}_2]_{15}\text{NH}$ is a powerful local anæsthetic but its hydrochloride and acetate are very irritating. A similar but weaker action is shown by $[\text{CH}_2]_{14}\text{NH}$ but not by $[\text{CH}_2]_{16}\text{NH}$, $[\text{CH}_2]_{17}\text{NH}$, or $[\text{CH}_2]_{15}\text{NMe}$. $\alpha\chi$ -Dibromotetradecane is converted by $\text{o-C}_6\text{H}_4\text{C}(\text{CO})_2\text{NK}$ under N_2 at 180° into χ -bromotetradecylphthalimide, b.p. about $250^\circ/0.1 \text{ mm.}$, m.p. $68-69^\circ$ (corr.), hydrolysed to χ -bromotetradecylamine hydrobromide, m.p. $147-150^\circ$ (corr.), which is transformed by NaOH in Pr^iOH into tetradecamethyleneimine, b.p. $97-98^\circ/0.05 \text{ mm.}$, m.p. $47-48^\circ$ (corr.) (yield 42%), χ -hydroxytetradecylamine, m.p. $83-84^\circ$ (corr.) [hydrochloride; carbamide derivative, $\text{C}_{15}\text{H}_{32}\text{O}_2\text{N}_2$, m.p. $103-104^\circ$ (corr.)] (yield 21%), and dimeric products [dihydrobromide, $\text{C}_{18}\text{H}_{40}\text{N}_2\text{Br}$, m.p. about 215° (corr.; decomp.)] (yield 24%). ν -Bromotridecylphthalimide, b.p. about $230^\circ/0.1 \text{ mm.}$, m.p. $54-55^\circ$ (corr.), is hydrolysed to γ -bromotridecylamine [hydrobromide, m.p. 155° (corr.)], whence tridecamethyleneimine, b.p. $65^\circ/0.05 \text{ mm.}$, m.p. $38-39^\circ$ (corr.) [hydrochloride, m.p. $150-151^\circ$ (corr.)], ν -hydroxytridecylamine, m.p. 84° (corr.), and the dimeride [dihydrochloride, m.p. $>300^\circ$; $(\text{NO})_2$ -derivative, m.p. $86-$

87°]. λ -Bromoundecylphthalimide, b.p. about 200—210°/0.1 mm., m.p. about 43° (corr.), yields λ -bromoundecylamine hydrobromide, m.p. 154—155° (corr.), from which little if any of the corresponding cyclic imine could be obtained; λ -hydroxyundecylamine hydrochloride, m.p. 145° (corr.), and the dihydrochloride, $C_{22}H_{48}N_2Cl_2$, decomp. >250°, of the dimeric base are described. λ -Iodoundecylamine hydrochloride has m.p. 139—140° (corr.). π -Bromohexadecylamine hydrobromide yields hexadecamethyleneimine, m.p. 58—59° (corr.), π -hydroxyhexadecylamine, m.p. 90—91° (corr.) [hydrochloride, m.p. 152—153° (corr.)], and very little dimeride. The following substances are incidentally described: octamethyleneimine platinichloride, m.p. 187—188° (corr.); trimethyleneimine, b.p. 62°/730 mm.; methyl-pentadeca-, b.p. 93—95°/0.05 mm. [picrate, m.p. 93—94° (corr.); hydrochloride, m.p. 215—216° (corr.)], obtained by means of CH_2O and HCO_2H , -penta-, b.p. 103—105°/724 mm., -octa-, b.p. 62—63°/16 mm., -hexadeca-, b.p. 124—127°/0.25 mm., and -heptadeca-methyleneimine, b.p. 126—129°/0.05 mm. H. W.

Compounds of nitroprussides and hexamethylenetetramine. E. VOYATZAKIS (Compt. rend., 1936, 203, 1365—1367).—An alkali or alkaline-earth salt in conc. solution with $(CH_2)_6N_4$ and Na nitroprusside affords compounds, $M^{II}Fe(CN)_5 \cdot NO \cdot 2(CH_2)_6N_4 \cdot xH_2O$ [$M^{II} = Ca (x = 8), Sr (x = 6), Ba (x = 4), Mg (x = 7), K_2 (x = 3), Na_2 (x = 4), and Li_2 (x = 3)$], whereas in dil. solutions $M^{II}Fe(CN)_5 \cdot NO \cdot (CH_2)_6N_4 \cdot xH_2O$ [$M^{II} = Ca (x = 4), Sr (x = 5), and Mg (x = 6)$] are formed. These compounds are stable in air and are decomposed by acids. J. L. D.

Acetyltrideuterocholine. H. ERLNMEYER and H. LOBECK (Helv. Chim. Acta, 1937, 20, 142—143).—The action of K—Na on a solution of $CCl_3 \cdot CO_2K$ in D_2O gives $CD_3 \cdot CO_2K$, whence $CD_3 \cdot COCl$, b.p. 47—51°, and trideuteroacetylcholine bromide, $CD_2 \cdot {}^{64}H_{1036} \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot NMe_3Br$, which is distinctly less active physiologically than choline. H. W.

Reduction products from sugars and aliphatic amines. P. KARRER and E. HERKENRATH (Helv. Chim. Acta, 1937, 20, 83—86).—Treatment of glucose with anhyd. NH_2Me at room temp. and hydrogenation (Pd on norite) of the product at 60°/23 atm. gives *N*-methyl-1-glucosamine, $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CH_2 \cdot NHMe$, m.p. 126°, $[\alpha]_D^{18} = -18.5^\circ \pm 1.0^\circ$ in H_2O , transformed by MeI in boiling $EtOH$ into trimethyl-d-sorbitylammonium iodide, m.p. 111°, *N*-Ethyl-1-d-glucosamine, m.p. 137°, $[\alpha]_D^{18} = -17.0^\circ \pm 1.0^\circ$ in H_2O , gives a hydrobromide, m.p. 108°. *N*-Ethyl-d-1-galactosamine, m.p. 145.5°, $[\alpha]_D^{18} = -6.3^\circ \pm 1.0^\circ$ in H_2O , and *N*-methyl-d-mannosamine, m.p. 135°, $[\alpha]_D^{18} = +8.2^\circ \pm 1.0^\circ$ in H_2O , are obtained analogously, whereas arabinose affords di-1-arabitylamine, m.p. 172°, $[\alpha]_D^{18} = -10.2^\circ \pm 1.0^\circ$ in H_2O (hydrochloride, m.p. 200°). H. W.

Derivatives of phenylglucosamine. P. KARRER and E. SALOMON (Helv. Chim. Acta, 1937, 20, 90—96).—Phenylglucosamine (I), $CH_2Cl \cdot CO_2H$, and Na_2CO_3 in boiling H_2O give *Na* phenylglucosaminooacetate, $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CH_2 \cdot NPh \cdot CH_2 \cdot CO_2Na (+1H_2O)$, m.p. 120—130° and, after re-solidification, m.p. 210—

212°. Phenylglucosaminooacetic acid, m.p. 139—140° (decomp.), readily loses CO_2 with formation of phenylmethylglucosamine, $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CH_2 \cdot NPhMe$, m.p. 150—151°. If (I) is heated with $CH_2Cl \cdot CO_2H$ and only sufficient Na_2CO_3 to neutralise the liberated HCl , phenylglucosaminooacetolactone, $CH_2 \cdot \begin{matrix} NPh \cdot CH_2 \\ \diagup \quad \diagdown \\ CO \quad O \end{matrix} > CH \cdot [CH \cdot OH]_3 \cdot CH_2 \cdot OH$, m.p. 205—206°, is produced. Gradual addition of I to a solution of (I) and $KHCO_3$ in H_2O gives *p*-iodophenylglucosamine, which with $CH_2Cl \cdot CO_2H$ and Na_2CO_3 affords *Na* *p*-iodophenylglucosaminooacetate, m.p. 228—230°, also $+1H_2O$, m.p. (indef.) 130—140°, and $+1EtOH$; the corresponding free acid appears to break down immediately into CO_2 and *p*-iodophenylmethylglucosamine, decomp. 152° after becoming blue at 140°. H. W.

Amino-acids, acyl-amino-acids, dipeptides, acyl-dipeptides, and derivatives of these compounds. II. Effects of irradiation with cathode rays and ultra-violet light. A. J. ALLEN, R. E. STEIGER, M. A. MAGILL, and R. G. FRANKLIN (Biochem. J., 1937, 31, 195—204).—By spectroscopic examination, it was found that solutions of several NH_2 -acids, dipeptides, and derivatives in H_2O or 95% $EtOH$ undergo a change when irradiated by cathode rays or ultra-violet light regardless of whether the constituent NH_2 -acids are primary, *sec.*, or *tert.* NH_3 is liberated in every case. Possible reaction mechanisms are given. The absorption curves of acetyl-dipeptides are shifted towards the red by ultra-violet light and cathode rays, and the effect of the latter on acetyl-dipeptides in which the OH of the CO_2H is replaced by $NHPh$ is usually < that on the free acid. J. N. A.

Detection and colorimetric determination of glycine with the alloxan reagent. G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1935, 73, 161—168; Chem. Zentr., 1936, i, 2153).—Details of a colour reaction are given. H. N. R.

Micro-crystal reaction of glycine. G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1935, 73, 168—172; Chem. Zentr., 1936, i, 2153).—A reaction with phosphotungstic acid is described. H. N. R.

Diamino-acid, canavanine. V. Synthesis of canaline. M. KITAGAWA (J. Biochem. Japan, 1936, 24, 107—112; cf. A., 1936, 1236).— α -Amino- γ -hydroxybutyric acid (A., 1934, 61) yields a Bz derivative, m.p. 140—144°, which in 1% HCl at 70° affords the corresponding lactone, m.p. 139°, $[\alpha]_D^{17} = -28^\circ$ in $EtOH$, which with $HI \cdot EtOH$ gives *Et* γ -iodo- α -benzamidobutyrate, m.p. 119—120°; with benzhydroxamic acid, this substance affords $NHBz \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(NHBz) \cdot CO_2Et$, hydrolysed (10% HCl) to canaline, which is therefore $NH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$. F. O. H.

Heptyl carbamidoacetate, m.p. 98—99°, and α -carbamidohexanoate, m.p. 70—71°, and heptyl ester, m.p. 123—125° of carbamidoacetylglutamine. —See A., I, 134.

Methods of hydrolysis of protein: shortening the time for determining cystine. M. X. SUL-

LIVAN and W. C. HESS (J. Biol. Chem., 1937, 117, 423—428).—The protein is hydrolysed by aq. HCl in the presence of TiCl_3 , which lessens humin formation, and decreases the time necessary for cysteine (I) liberation. (I) may be determined directly, or after oxidation to cystine. F. A. A.

N-Substituted aliphatic amides. G. F. D'ALELIO and E. E. REID (J. Amer. Chem. Soc., 1937, 59, 111—112).—The following $\text{AlkCO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, $\text{AlkCO}\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, and $\text{AlkCO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ are prepared from AlkCO_2Et and the NH_2 -alcohols at the b.p. (lower members) or 160° : form-, b.p. $150\text{--}155^\circ/2$ mm., acet-, b.p. $155\text{--}160^\circ/2\text{--}3$ mm., m.p. 40° (lit. $63\text{--}65^\circ$), propion-, b.p. $160\text{--}168^\circ/1\text{--}2$ mm., butyr-, b.p. $155\text{--}162^\circ/1\text{--}1.5$ mm., valer-, b.p. $192^\circ/6$ mm., m.p. 32° , hexo-, m.p. 46° , hepto-, m.p. 53.6° , octo-, m.p. 63.2° , nono-, m.p. 71.6° , deco-, m.p. 77.1° , undeco-, m.p. 84.8° , dodeco-, m.p. 78.2° , trideco-, m.p. 91.8° , tetradeco-, m.p. 87.4° , pentadeco-, m.p. 97° , hexadeco-, m.p. 94.4° , heptadeco-, m.p. 99.2° , and octadeco-, m.p. 96.1° , β -hydroxyethylamides; undeco-, m.p. 34.9° , dodeco-, m.p. 38.7° , trideco-, m.p. 45.3° , tetradeco-, m.p. 47.9° , pentadeco-, m.p. 50.9° , hexadeco-, m.p. 65.1° , heptadeco-, m.p. 67.9° , and octadeco-, m.p. 69.7° , $\beta\beta'$ -dihydroxydiethylamides; nono-, m.p. 53.8° ; deco-, m.p. 58.1° , undeco-, m.p. 63.1° , dodeco-, m.p. 66.6° , trideco-, m.p. 71° , tetradeco-, m.p. 74.2° , pentadeco-, m.p. 75.1° , hexadeco-, m.p. 78.2° , heptadeco-, m.p. 82° , and octadeco-, m.p. 86.1° , β -hydroxypropylamides. H. B.

N-Methylamides [of fatty acids]. G. F. D'ALELIO and E. E. REID (J. Amer. Chem. Soc., 1937, 59, 109—111).— $\text{HCO}\cdot\text{NHMe}$, b.p. $131^\circ/90$ mm., m.p. -5.4° (hydrochloride, m.p. $82.8\text{--}85^\circ$), and NHMeAc , b.p. $140.5^\circ/90$ mm., m.p. 28° (hydrochloride, m.p. $67.2\text{--}69.4^\circ$; N-Br-, m.p. 123.5° , -NO-, b.p. 116.3° , m.p. -8.5° , and -Ac, b.p. 194.2° , m.p. -46.8° , derivatives), are prepared (method: A., 1931, 831) from the acid and NH_2Me . The following are obtained by addition of the acid chloride to conc. aq. NH_2Me (3 mols.) at -20° to room temp.: propion-, b.p. $146^\circ/90$ mm., m.p. -43° (hemihydrochloride, m.p. $84\text{--}85^\circ$), butyr-, b.p. $156^\circ/90$ mm., m.p. -5.2° (hemihydrochloride, m.p. $106.4\text{--}108^\circ$), valer-, b.p. $169^\circ/90$ mm., m.p. -25.5° (hemihydrochloride, m.p. $17\text{--}20^\circ$), hexo-, b.p. $183^\circ/90$ mm., m.p. 13.6° (hemihydrochloride, m.p. -1° to 3°), hepto- (I), b.p. $151^\circ/15$ mm., m.p. 14° (lit. 9°) (hemihydrochloride, m.p. $32\text{--}34^\circ$), octo- (II), b.p. $161.5^\circ/15$ mm., m.p. 38.9° (hemihydrochloride, m.p. $38\text{--}40^\circ$), nono- (III), b.p. $175^\circ/15$ mm., m.p. 39.1° , deco-, m.p. 57.3° , undeco-, m.p. 56° , dodeco-, m.p. 68.4° , trideco-, m.p. 68.2° , tetradeco-, m.p. 78.4° , pentadeco-, m.p. 78.3° , hexadeco-, m.p. 85.5° , heptadeco-, m.p. 84.8° , and octadeco-, m.p. 92.1° , -methylamides. The m.p. alternate similarly to those of the corresponding acids. (I)—(III) are local anaesthetics. H. B.

[Thiocyanogen and its addition to unsaturated fatty acids.] L. BIRCKENBACH and J. GOUBEAU (Ber., 1937, 70, [B], 171).—A question of priority against Kaufmann and Oetringhaus (this vol., 47).

H. W.

Determination of thiocarbamide. R. CUTHILL and C. ATKINS (J.S.C.I., 1937, 56, 5—8T).—The re-

actions of $\text{CS}(\text{NH}_2)_2$ with various oxidising agents in solution have been studied. Oxidation with I in alkaline solution, $\text{Ce}(\text{SO}_4)_2$, or $\text{K}_2\text{Cr}_2\text{O}_7$ may be utilised for determination, the $\text{CS}(\text{NH}_2)_2$ being oxidised to $\text{CO}(\text{NH}_2)_2$ and H_2SO_4 . Another method of determination depends on the reaction of $\text{CS}(\text{NH}_2)_2$ with excess of standard AgNO_3 in ammoniacal solution, forming Ag_2S and $\text{CO}(\text{NH}_2)_2$. After reaction, the mixture is acidified with HNO_3 and filtered, the excess of AgNO_3 in the filtrate being titrated with standard KCNS solution. R. C.

$\beta\gamma$ -Ethylenic nitriles and their derivatives. R. DELABY (Compt. rend., 1936, 203, 1521—1523).—Vinyl-laurylcarbinol, m.p. $27\text{--}28^\circ$, vinyl-isobutyl-, -sec-octyl-, and $\beta\zeta$ -dimethyloctyl-carbinol are prepared as described previously (A., 1933, 808). These and other similar compounds are converted by PBr_3 into allyl bromides (I) (cf. A., 1928, 1112), the straight-chain more easily than the branched, which consist mainly of the *trans*-isomerides (cf. A., 1935, 197). (I) with $\text{Cu}(\text{CN})_2$ (cf. A., 1922, i, 817) afford allyl nitriles, converted by boiling 50% H_2SO_4 into γ -lactones and thence with dil. NaOH or $\text{Ba}(\text{OH})_2$ into $\beta\gamma$ -unsaturated acids. Acids $> \text{C}_{10}$ are not obtained pure as they are isomerised to the $\alpha\beta$ -unsaturated form by the more severe conditions necessary for the hydrolysis. J. L. D.

Maleo- and fumaro-nitriles. J. JENNEN (Bull. Acad. roy. Belg., 1936, [v], 22, 1169—1184).—When heated with CuCN at $165\text{--}170^\circ$, *cis*- $\text{C}_2\text{H}_2\text{I}_2$ affords maleonitrile (I), m.p. $32.2\text{--}32.6^\circ$, together with some fumaronitrile (II), m.p. $96\text{--}96.4^\circ$, obtained from the *trans*- $\text{C}_2\text{H}_2\text{I}_2$ formed by thermal isomerisation. Hydrolysis of (I) with H_2SO_4 (*d* 1.84) affords the corresponding diamide but (II) gives maleamic acid. At 13° 0.1N-NaOH eliminates 1 mol. of HCN from 2 mols. of either (I) or (II) [more rapidly from (I)], but the reaction is more complex at higher temp. The *d* and *n* vals. at various temp. are recorded: the [*M*] exaltation for (I) and (II) is approx. double that for isocrotono- and crotono-nitrile, respectively. J. W. B.

Maleo- and citracono-nitriles. P. BRUYLANTS and J. JENNEN (Bull. Acad. roy. Belg., 1936, [v], 22, 1141—1143).—By comparison with the genuine nitriles (preceding abstract) the supposed maleo- and citracono-nitrile obtained by the action of P_2O_5 on the amides (de Wolf *et al.*; van de Straete, A., 1935, 737) are shown to be the *imide*, only 1 mol. of NH_3 being eliminated in these cases. With fumar- and mesacon-amide normal nitrile formation occurs. J. W. B.

Pyrophosphoric ester and crystallised salts of *l*-phospholactic acid. T. WAGNER-JAUREGG and H. GRIESSHABER (Ber., 1937, 70, [B], 8—11).—Pyrophosphoryl chloride (I), b.p. $73^\circ/1$ mm., $88\text{--}92^\circ/8$ mm., best obtained by the action of nitrous fumes on PCl_3 at 0° , does not appear to react smoothly with muscled-adenylic acid (in presence of H_3BO_3) or $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ in $\text{C}_5\text{H}_5\text{N}$; the method is unsuited to the prep. of unsymmetrical esters. Brucine hydrochloride and K *l*-phospholactate give the salt, $\text{C}_3\text{H}_7\text{O}_6\text{P}\cdot(\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_3)\cdot 12\text{H}_2\text{O}$, m.p. $153\text{--}154^\circ$ (corr.; block), whilst Ba *l*-phospholactate and brucine sul-

phate in H_2O afford the compound, $\text{C}_3\text{H}_7\text{O}_6\text{P}(\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2)_2 \cdot 4\text{H}_2\text{O}$, anhyd. m.p. 166° (corr.; block), $[\alpha]_D^{25} -29.7^\circ$ in H_2O , transformed into the corresponding Ba salt, $[\alpha]_D^{25} -13.6^\circ$ in 2N-HCl. *Acridinium 1-phospholactate*, m.p. $269-271^\circ$ (sealed tube), is described. H. W.

Preparation of phosphoglyceric and glycerophosphoric acids by decomposition of hexose diphosphate by yeast.—See A., III, 70.

Reducing action of metal alkyls, especially of aluminium and boron alkyls. H. MEERWEIN, G. HINZ, H. MAJERT, and H. SÖNKE (J. pr. Chem., 1936, [ii], 147, 226—250).—Aldehydes ($\text{R}\cdot\text{CHO}$) and ketones, when heated with AlEt_3 in Et_2O (A., 1923, i, 289) and then treated with dil. H_2SO_4 , are reduced to the corresponding alcohol with evolution of C_2H_4 , or alkylated and converted into the alcohol $\text{CHREt}\cdot\text{OH}$, the relative proportions of these alcohols depending on the nature of the aldehyde or ketone. Thus, chloral, bromal, $\text{COPh}\cdot\text{CCl}_3$, mono- and tri-chloroacetone give the corresponding alcohol in good yield, benzil gives benzoin (yield 40%), but $\text{R}\cdot\text{CHO}$ ($\text{R} = \text{Ph}$, $p\text{-C}_6\text{H}_4\text{Cl}$, $p\text{-OMe}\cdot\text{C}_6\text{H}_4$, and $\text{CHPh}\cdot\text{CH}\cdot$) gives mainly the alcohol $\text{CHREt}\cdot\text{OH}$. The colorations formed when the foregoing aldehydes and ketones are mixed with $\text{AlEt}_3\text{-Et}_2\text{O}$ are recorded, and their formation supports the view that additive complexes are first formed. With BEt_3 reaction occurs less readily, and only the corresponding alcohol is formed, no alkylation taking place. The primary product of the reaction is an ester of diethylboric acid and is readily hydrolysed by H_2O to the alcohol. The following esters of $\text{BEt}_2\cdot\text{OH}$ have thus been prepared: $\beta\beta\beta$ -trichloroethyl (I), b.p. $78-79^\circ/12$ mm.; benzyl, b.p. $114-115^\circ/16$ mm.; and p -chlorobenzyl, b.p. $141.5-142^\circ/16$ mm. $\text{BEt}_3\text{-Et}_2\text{O}$ with bromal at $35-40^\circ$ gives $\beta\beta\beta$ -tribromoethyl diethylborate (II), b.p. $117-119^\circ/12$ mm.; at 90° , however, the main product is dibromovinyl diethylborate, $\text{BEt}_2\cdot\text{O}\cdot\text{CH}\cdot\text{CBr}_2$ (III), b.p. $98-99^\circ/11$ mm. (decomposed by H_2O to $\text{CHBr}_2\cdot\text{CHO}$, H_2O), and some EtBr , and with excess of bromal at 120° the main product is a mixture of di(dibromovinyl) ethylborate, $\text{BEt}(\text{O}\cdot\text{CH}\cdot\text{CBr}_2)_2$ (IV), b.p. $140-143^\circ/3$ mm., and a little dibromovinyl $\beta\beta\beta$ -tribromoethyl ethylborate, $\text{BEt}(\text{O}\cdot\text{CH}\cdot\text{CBr}_2)\cdot\text{CH}_2\cdot\text{CBr}_3$ (V). (IV) and a little (V) are also obtained from (III) and bromal at 120° , and (V) and a little di-($\beta\beta\beta$ -tribromoethyl) ethylborate, $\text{BEt}(\text{O}\cdot\text{CH}_2\cdot\text{CBr}_3)_2$ from (II) and bromal at 135° . These reactions occur with evolution of C_2H_4 or EtBr . The esters (I) and (II) were also obtained directly from the appropriate alcohol and BEt_3 . ZnEt_2 and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ give $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and some $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHEt}\cdot\text{OH}$, whilst MgEtBr gives the latter product only. No reaction occurs between SnEt_4 and chloral or bromal. The foregoing results support the view that the tendency for alkylation to occur instead of simple reduction increases with increasing electropositive character of the metal (cf. this vol., 83).

H. G. M.

Diethylboric acid. H. MEERWEIN and H. SÖNKE (J. pr. Chem., 1936, [ii], 147, 251—255).—Diethylboric acid (I), m.p. -51° to -48° , b.p. $35-37^\circ/75$ mm. (cf. J.C.S., 1876, 469), is best prepared by hydrolysis of its p -chlorobenzyl ester (see above)

with H_2O , followed by high-vac. distillation. It is not spontaneously inflammable, and when distilled at atm. pressure decomposes partly to diethylboron oxide, $(\text{BEt}_2)_2\text{O}$, b.p. $142-144^\circ$, the temp. rising from about 80° to 150° . Diethylboracetate, m.p. $86-87^\circ$, and diethylbor-*o*-chlorobenzoate, m.p. $50-52^\circ$, b.p. $96-97^\circ$, are obtained when BEt_3 is mixed with the appropriate acid. (I) can be titrated in $\text{MeOH-H}_2\text{O}$ in presence of mannitol as a monobasic acid; a quadricovalent salt of the type $[\text{BEt}_2(\text{OH})(\text{OMe})]\text{M}$ ($\text{M} = \text{univalent metal}$) is formed, but could not be isolated. Contrary to the observations of Frankland (Ann. Chem., 1862, 124, 137) BEt_3 continues to react with acids, evolving C_2H_6 , after the first Et has been replaced; and intermediate products in the progressive autoxidation of BEt_3 to $\text{B}(\text{OEt})_3$ could not be isolated. H. G. M.

Free radicals in the dissociation of gaseous metal alkyls by light.—See A., I, 145.

Disymmetrical synthesis in the case of complex metallic salts. II. I. LIFSCHITZ (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 1192—1199).—Glutamic acid or Na monoglutamate (I) on boiling with $\text{Co}(\text{OH})_3$ yields a mixture of the α - and β -D-modifications of the acid $[\text{Co}(d\text{-glut.})_3]\text{H}_3$ (II) (glut. = $\text{NH}_2\cdot\text{CH}(\text{CO}_2\cdot)[\text{CH}_2]_2\text{CO}_2$) and its Na salt. These are separable through the Ag and Pb salts of the red β -form being insol., and those of the violet α -form sol., in boiling H_2O . These are reconvertible into the very sol. Na salts by NaCl and Na_2SO_4 solutions. If, however, an aq. solution of $\text{Co}(\text{NO}_3)_2$ (1 mol.), (I) (3 mols.), and NaOH (2 mols.) is oxidised by a current of air at room temp., a similar violet solution is obtained containing the α - and β -L-forms of (II). These are separable through the Ag salt of the violet α -form being sol., and that of the red β -form insol., in hot H_2O but yielding a dull red compound $[\text{Co}(d\text{-glut.})_3][\text{Ag}(\text{C}_6\text{H}_5\text{N})_2]_3$ with aq. $\text{C}_6\text{H}_5\text{N}$. The rotatory dispersions of these compounds, which lead to the assignment of the constitutions given above, are shown in graphical form. J. W. S.

Theory of isomerisation of cyclic compounds.

A. A. NIKOLAEV (J. Gen. Chem. Russ., 1936, 6, 1587—1592).—Theoretical. R. T.

Synthesis of mono-substituted homologues of cyclopentane with branched side-chains. B. A. KAZANSKI, A. F. PLATE, and K. M. GNATENKO (J. Gen. Chem. Russ., 1936, 6, 1593—1597).—*iso*Propyl-, *sec*-butyl-, *sec*-amyl-, b.p. $174-176^\circ$, and benzhydryl-cyclopentane, m.p. $32.5-33^\circ$, were obtained by catalytic hydrogenation (Pt or Pd) of dimethyl-, methyl-ethyl-, diethyl-, or diphenyl-fulvene, respectively. R. T.

Action of aluminium chloride on dicyclohexyl. J. K. JURIEV, P. J. LEVINA, and A. I. KUDRJAVCEV (J. Gen. Chem. Russ., 1936, 6, 1500—1505).—Dicyclohexyl, obtained in good yield from Ph_2 and H_2 ($\text{Ni-Al}_2\text{O}_3$ catalyst at $100^\circ/90$ atm.), when heated at $160-290^\circ$ in presence of AlCl_3 yields a mixture of methylcyclohexane, cyclopentane, EtPr^s , and CMe_4 . R. T.

Mechanism of irreversible catalysis of unsaturated cyclic hydrocarbons with a double

linking in the side-chain. P. J. LEVINA, D. A. PETROV, and D. M. TRACHTENBERG (J. Gen. Chem. Russ., 1936, 6, 1496—1499).—The mixtures cyclohexane-diallyl, methylcyclohexane- Δ^2 -heptene, and dimethylcyclohexane- Δ^2 -isooctene and -allylbenzene are converted by Pt-C catalyst at 200—300° into saturated products. Formation of cyclohexenes as intermediate products is postulated. R. T.

Effect of structure on the reactions of benzene derivatives.—See A., I, 142.

Slow combustion of benzene.—See A., I, 141.

Determination of small concentrations. XIII. Determination of benzene. S. I. SINIAKOVA (J. Appl. Chem. Russ., 1936, 9, 2109—2115).— C_6H_6 (≤ 0.6 mg.) is nitrated with Stepanov's mixture, the m - $C_6H_4(NO_2)_2$ (I) produced is extracted with Et_2O , and dissolved in 2 ml. of $COMe_2$; 5 drops of 5% $NaOH$ are added, followed after 15 min. by 1 ml. of H_2O , and the violet coloration is compared with that given by standard (I). R. T.

Cleavage of side-chains in aromatic hydrocarbons in the form of paraffins by means of aluminium chloride. V. N. IPATIEV and H. PINES (J. Amer. Chem. Soc., 1937, 59, 56—60).— $PhPr^{\beta}$, $PhBu$ -*sec.*, $PhBu^{\gamma}$, and *sec.*-amylbenzene with $AlCl_3$ - HCl in cyclohexane (I) or, better, decahydronaphthalene at 65—80° give C_3H_8 (also formed from p - $C_6H_4Pr^{\beta}_2$), n - C_4H_{10} , *iso*- C_4H_{10} , and *isopentane*, respectively. The case of fission is $Bu^{\gamma} > sec$ - $Bu > Pr^{\beta}$. Similar fission does not occur with $PhMe$ and $PhEt$. Pr^{β} is eliminated more readily from $PhPr^{\beta}$ in (I) than in methylcyclohexane; fission does not occur in 4-methylisopropylcyclohexane. During the above reactions (I) is probably converted into phenylcyclohexane; side reactions also occur. H. B.

Microcolorimetric determination of toluene. W. P. YANT, S. J. PEARCE, and H. H. SCHRENK (U.S. Bur. Mines, 1936, Rept. Invest. 3323, 12 pp.).—After nitration (fuming HNO_3) of $PhMe$, dilution, and neutralisation, the $COMeEt$ extract with 50% aq. KOH develops a reddish-blue colour which is matched against standards similarly prepared. C_6H_6 does not interfere, and an accuracy of $\pm 10\%$ is obtained between 0.05 and 0.25 mg. of $PhMe$. Operative details are given. F. N. W.

Electrochemical oxidation of benzene homologues. VII. ψ -Cumene. F. FICHTER and G. SCHETTY (Helv. Chim. Acta, 1937, 20, 150—156; 1935, 1229).—Using a Pb anode in presence of dil. H_2SO_4 the main reaction product is CO_2 . Small amounts of xylylaldehyde, xylic acids, methylterephthalic acid, xyleneol, toluquinone, resin, $AcOH$, and HCO_2H are also formed. E. S. H.

Steric influences on the phenomenon of mesomerism. R. H. BIRTLES and G. C. HAMPSON (J.C.S., 1937, 10—15).—If the discrepancies between the observed moments of p -disubstituted C_6H_6 derivatives and those calc. by assuming vector addition are due to resonance involving quinonoid structures, then with substituents such as NH_2 , NO_2 , NMe_2 , OMe there should be a tendency for the H, O, or Me of these groups to be held in the plane of the ring, but

the introduction of Me in *o*-positions should exert a steric effect opposing this tendency. The dipole moments of nitro-, amino- (I), nitroamino-, bromonitro-, and dinitro-durene (II), and $C_6Me_5NH_2$ are $<$ those of the corresponding C_6H_5 derivatives. The conclusion is reached that the lowering of the moment is due to a damping of the resonance by the steric effects of the Me groups. Bromodurene, in which no steric effect is expected, has almost the same moment as $PhBr$. Bromoaminodurene (II), m.p. 138.5—139.5°, is obtained from (I) by Br in $AcOH$.

J. D. R.

Mononitration of *o*-chloriodobenzene. G. WALLAGH and J. P. WIBAUT (Rec. trav. chim., 1936, 55, 1071—1081).—Reduction ($TiCl_3$) of 1:2:6- $C_6H_3Cl(NO_2)_2$ [from 2:6- $(NO_2)_2C_6H_3NH_2$ by Sandmeyer's method] gives 2-chloro-3-nitroaniline, m.p. 95—96°, which after diazotisation reacts with KI to form 1-chloro-2-iodo-6-nitrobenzene, m.p. 59.8°, whilst diazotisation of 2:1:3- $NH_2C_6H_3ClNO_2$ followed by KI affords 1-chloro-2-iodo-3-nitrobenzene, m.p. 100—101°. Nitration (HNO_3 , *d* 1.52; 1 hr. at -5° followed by 1 hr. at 0°) of *o*- C_6H_4ClI gives 17.2% of 1:2:3-, 30.1% of 1:2:4-, 42.5% of 1:2:5-, and 10.3% of 1:2:6- NO_2 -derivatives (thermal analysis). The results are discussed in connexion with Holleman and Wibaut's rule (A., 1913, i, 169). F. N. W.

Mobility of the iodoxy-group in *p*-iodoxy-nitrobenzene. D. VORLÄNDER [with H. DAVID] (Ber., 1937, 70, [B], 146—151).—The behaviour of p - $NO_2C_6H_4IO_2$ towards boiling H_2O , aq. $NaNO_2$, and aq. NaN_3 shows that in very varied reactions IO_2 is less firmly bound than NO_2 to the C_6H_4 nucleus. This is ascribed to the more strongly active, unsaturated character of IO_2 in contrast with the more turgid NO_2 and to the peculiar relationships of I to O which may be so pronounced that the influence of NO_2 on IO_2 is almost completely suppressed as in the reaction with alkalis. The mobility of IO_2 in the reaction between $NO_2C_6H_4IO_2$ and neutral salts is so increased by a second *o*- NO_2 that changes occur with 2:4- $(NO_2)_2C_6H_3IO_2$ at 15—20° which do not occur below 90—100° with p - $NO_2C_6H_4IO_2$. The chemical process here, apart from external conditions, depends on the C_6H_4 derivative, and on the nature of the reaction partner and the products of the change. Although the reversal of the change or the establishment of an equilibrium between the partners of org. and inorg. origin cannot be fully demonstrated, the concn. of the solution and the action of mass are influential. It is not immaterial whether IO_3 separates as sparingly sol. $AgIO_3$ or $Ba(IO_3)_2$ or remains in solution as freely sol. alkali iodate. The charges, however, are not ionic in character. When NO_2 and IO_2 are in the *ortho* position steric influences may come into play similar to those observed by Lock in the cases of aromatic aldehydes and alkali hydroxides. The ready mobility of IO_2 in 2:4- $(NO_2)_2C_6H_3IO_2$ and of 1- NO_2 in 1:2:4- $C_6H_3(NO_2)_3$ is probably due to co-operation of energy contrasts with steric relationships. H. W.

Mobility of the iodoxy-group in 1-iodoxy-2:4-dinitrobenzene. H. LÜTGERT (Ber., 1937, 70,

[B], 151—157).—2:4-(NO₂)₂C₆H₃·IO₂ is best obtained by the oxidation of 1:2:4-C₆H₃I(NO₂)₂ with HOCl in AcOH, whereby 2:4-(NO₂)₂C₆H₃·IO is possibly formed intermediately. It is readily and almost quantitatively converted by aq. NaOH into *m*-C₆H₄(NO₂)₂ and NaIO₃. Aq. AgNO₃ reacts readily: (NO₂)₂C₆H₃·IO₂ + AgNO₃ + H₂O = *m*-C₆H₄(NO₂)₂ + AgIO₃ + HNO₃, whereas with H₂O at 15—20° the change is not appreciable after several weeks. *m*-C₆H₄(NO₂)₂ is not converted by HIO₃ in H₂O or conc. H₂SO₄ into (NO₂)₂C₆H₃·IO₂. 2:4-(NO₂)₂C₆H₃·IO₂ and conc. aq. NH₃ give mainly *m*-C₆H₄(NO₂)₂ with some 1:2:4-C₆H₃I(NO₂)₂, which give an adduct (1:1), m.p. 64—67°. With aq. NaNO₂ at 15—20°, 2:4-(NO₂)₂C₆H₃·IO₂ yields 1:2:4-C₆H₃(NO₂)₃ with some 2:4-(NO₂)₂C₆H₃·OH; the latter is the main product in hot solution, being possibly formed by hydrolysis of 1:2:4-C₆H₃(NO₂)₃. NaN₃ and 2:4-(NO₂)₂C₆H₃·IO₂ yield 2:4-(NO₂)₂C₆H₃·N₃; it appears impossible to isolate the expected iodo-base, which becomes disproportionated to I' or I and IO₃'. If NaNO₂ is replaced by AgNO₂ at 15—20° the product is 1:2:4-C₆H₃(NO₂)₃ with approx. 1 mol. of AgI and 2 mols. of AgIO₃. With aq. NaNO₂ or Ba(NO₂)₂ free I is liberated. 2:4-(NO₂)₂C₆H₃·IO₂ is moderately stable towards dil. and conc. HNO₃, conc. H₂SO₄ and H₂SO₄ + HNO₃. HCl gives free Cl₂ and C₆H₃I(NO₂)₂. Dil. AcOH at 15—20° causes the change: (NO₂)₂C₆H₃·IO₂ + H₂O = (NO₂)₂C₆H₃·OH + HIO₂. In the acid medium HIO₂ becomes transformed in an involved manner into IO₃' and used in iodinating (NO₂)₂C₆H₃·OH to 6-iodo-2:4-dinitrophenol.

H. W.

C·C linking in hexaphenylethane.—See A., I, 67.

Application of Ullmann's reaction to the preparation of dinaphthyls. H. H. HODGSON and R. L. ELLIOTT (J.C.S., 1937, 123—125).—The mechanism of the Ullmann reaction is discussed, with particular reference to the iodonitronaphthalenes, and the influence of the unsubstituted nucleus on the ease of removal of the I. With Cu in boiling PhNO₂, 3:1-C₁₀H₆I·NO₂ yields 4:4'-dinitro-2:2'-dinaphthyl, m.p. 316°, but similar treatment of 3:2-C₁₀H₆I·NO₂ affords only 2-C₁₀H₇·NO₂. 4:2-C₁₀H₆I·NO₂ in AcOH diazotised (conc. H₂SO₄) and treated with KI affords 1:4-di-iodo-2-nitronaphthalene (I), m.p. 126°, which with Cu in PhNO₂ yields 4:4'-di-iodo-3:3'-dinitro-1:1'-dinaphthyl, m.p. 275—280° (softening and decomp. at 220°, decomposed by slow heating to 220° to 3:3'-dinitro-1:1'-dinaphthyl), and 1:2-C₁₀H₇I·NO₂ (II). (I) fused with Cu at 180—210° yields 1:2-C₁₀H₆I·NO₂ and traces of (II). 1:2-Di-iodo-4-nitronaphthalene, m.p. 172° [from 4:2:1-NO₂·C₁₀H₅I·NH₂; prepared as (I)], with Cu in PhNO₂ is unchanged after 5 hr. boiling; after 10 hr. only 1-C₁₀H₇·NO₂ is obtained.

J. D. R.

Dissociable anthracene oxides. Photo-oxides of 9-phenyl-10-methyl- and of 9-phenyl-10-ethylanthracene. A. WILLEMART (Compt. rend., 1936, 203, 1372—1374).—9-Phenyl-10-methyl- (A., 1926, 1030) and -10-ethylanthracene (A., 1927, 881) in CS₂ when insolated afford photo-oxides, C₂₁H₁₆O₂ and C₂₂H₁₈O₂, which at 170° and 200°, respectively, evolve

20% and 35% of their O content, unlike the oxides of *meso*-diarylanthracenes (cf. A., 1935, 1233; 1936, 197, 462), but similarly to those of anthracene (A., 1935, 1488) and of 9-phenylanthracene (A., 1936, 1101).

J. L. D.

Bz-Monoalkylanthracenes. H. WALDMANN and E. MARMORSTEIN (Ber., 1937, 70, [B], 106—108).—Clemmensen's method is unsuited to the prep. of alkylanthracenes from the acyl compounds since the hydrides so formed are not readily dehydrogenated. Good results are obtained by application of the Wolff-Kishner method. 2-Ethylanthracene, m.p. 150—151° (picrate, m.p. 92°), is obtained by treating 2-acetylanthracene with N₂H₄·H₂O, NaOEt, and EtOH at 180°, or from 2-ethyl-9-anthrone by reduction with Zn dust and NH₃·H₂O. 2-Propionylanthracene affords 2-propylanthracene, m.p. 126° (picrate, m.p. 97°), oxidised by CrO₃ in AcOH to 2-propylanthraquinone. 2-isoPropylanthracene, m.p. 154—155° (picrate, m.p. 130—131°), is derived from 2-iso-propyl-9-anthrone. 1-Acetylanthracenesemicarbazone, decomp. 204—208°, is converted by a short treatment with NaOEt in EtOH at 180° into 1-ethylanthracene, m.p. 33—34° (picrate, m.p. 126—127°), whence 1-ethylanthraquinone, m.p. 96°.

H. W.

Hydrogenation of phenanthrene. J. R. DURLAND and H. ADKINS (J. Amer. Chem. Soc., 1937, 59, 135—137).—Pure phenanthrene (I) is reduced by H₂ and Cu-Cr oxide in EtOH at 150° to the 9:10-H₂-derivative (87%); at 220° the 1:2:3:4:5:6:7:8-H₂-derivative (II) is the main product (cf. Burger and Mosettig, A., 1936, 334). (II) is better prepared by reduction of (I) with H₂ + Raney Ni in methylcyclohexane at 120°; at about 200° tetradecahydrophenanthrene results.

H. B.

Synthesis of 1:2-benzanthracene derivatives related to cholanthrene. L. F. FIESER and M. S. NEWMAN (J. Amer. Chem. Soc., 1936, 58, 2376—2382).—1:2-Benzanthracenes containing Me at 5 and/or 10 could not be prepared by the modified Elbs reaction but are obtained by cyclisation and subsequent reduction of the appropriate 2-benzyl-1-naphthoic acids.

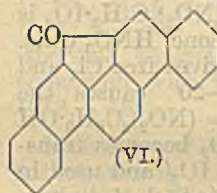
o-C₆H₄Me·MgBr (I) and 1:2-C₁₀H₆(CO)₂O (II) in boiling C₆H₆ give 38.43% of 2-*o*-toluoyl-1-naphthoic acid (III), m.p. 149.5—150.5° (Me ester, b.p. 215—216°/2.5 mm.), and about 3% of 1-*o*-toluoyl-2-naphthoic acid, m.p. 210—211°, which are decarboxylated at 230—245° in presence of a little of their Cu salts to *o*-tolyl β- and α-C₁₀H₇ ketone, respectively. (III) and MgMeBr (excess) in Et₂O-C₆H₆ afford 86% of the lactone, dimorphous, m.p. 103—104° and 119—120°, of 2-α-hydroxy-α:α-dimethylbenzyl-1-naphthoic acid, which is reduced (modified Clemmensen; Martin, A., 1936, 1249) to 2-α:α-dimethylbenzyl-1-naphthoic acid (IV), m.p. 183.5—184°. The crude anthrone from (IV) and conc. H₂SO₄ at 20° is reduced (Zn dust, 10% NaOH) to 5:10-dimethyl-1:2-benzanthracene (V), m.p. 147—147.5° (picrate, m.p. 173.7—174.2°). MgPhBr and (II) similarly give 30% of 2-benzoyl-1- (VI), m.p. 141.8—142.8°, and some 1-benzoyl-2-, m.p. 223.5—224.5°, -naphthoic acid. Me 2-benzoyl-1-naphthoate, m.p. 72.5—73.5° [from (VI) and CH₃N₂]; the "Me ester" obtained by Waldmann (A., 1931,

1063) using MeOH-HCl is probably the corresponding lactol Me ether, m.p. 156—156.5°, since it does not react with MgMeI, with MgMeI (1 equiv.) or, better, (VI) with MgMeBr affords the lactone, m.p. 173.8—174.2°, of 2- α -hydroxy- α -methylbenzyl-1-naphthoic acid; subsequent reduction (Clemmensen) gives 2- α -methylbenzyl-1-naphthoic acid, m.p. 128—129°, which is converted [as for (IV)] into 10-methyl-1:2-benzanthracene (VII), m.p. 140.2—140.8° (picrate, m.p. 173.5—174°). (III) is reduced by Mg octadecyl bromide to the lactone (VIII), m.p. 157—157.8°, of 2- α -hydroxy- α -methylbenzyl-1-naphthoic acid; MgEtBr (3 equivs.) affords (VIII) and some of the lactone, m.p. 124—125°, of 2- α -hydroxy- α -methyl- α -ethylbenzyl-1-naphthoic acid. Reduction (modified Clemmensen) of (VIII) yields 2- α -methylbenzyl-1-naphthoic acid, m.p. 144—145°, converted [as for (IV)] into 5-methyl-1:2-benzanthracene. Preliminary tests indicate that (V) has a carcinogenic activity of the same order as cholanthrene, methylcholanthrene, and 3:4-benzpyrene. (VII) is also carcinogenic.

β -C₁₀H₇, 2-ethyl-1-naphthyl ketone, b.p. 235—240°/2—2.5 mm. (from β -C₁₀H₇·COCl, 2-C₁₀H₇Et, and AlCl₃ in CS₂), heated at 425—430°/1.5 hr. gives 23% of 1:2:5:6-dibenzanthracene. *p*-Xylyl 2-ethyl-1-naphthyl ketone, b.p. 188—192°/2 mm. [from 2-C₁₀H₇Et and the chloride of 2:5-C₆H₃Me₂·CO₂H (prep. from 2:5-C₆H₃Me₂·COMe)], at 450—455°/15 min. afford (probably) a methylbenzanthracene, m.p. 124—126° (picrate, m.p. 155—156°). The carbinol from β -C₁₀H₇·COMe and (I) is dehydrated at 200—250° to α -*o*-tolyl- α -2-naphthylethylene, m.p. 66—66.5°, reduced (H₂, PtO₂, AcOH) to the ethane (IX), b.p. 177—179°/1.5—2 mm. Bromination (method: Cook and Haslewood, A., 1935, 1117) of (IX), subsequent treatment with C₆H₅N, conversion into the Grignard reagent, carbonation, and hydrogenation gives an acidic product which with 90% H₂SO₄ at 40° followed by Zn dust + alkali in PhMe affords a poor yield of a hydrocarbon, C₂₀H₁₆, m.p. 149—168° (picrate, m.p. 152—153°). Acetylation and chloroacetylation (Friedel-Crafts) of (IX) were unsuccessful. All m.p. are corr. H. B.

Dehydrogenation and ring-transformation of spiro-hydrocarbons. S. C. S. GUPTA (Current Sci., 1936, 5, 295—296).—cyclopentane-1-carboxylic-1-acetic anhydride with C₁₀H₈ and anhyd. AlCl₃ affords α -cyclopentyl- β -1, m.p. 140—141°, and β -2-naphthoylpropionic acid, m.p. 191°. The former is reduced (Clemmensen) to α -cyclopentyl- γ -1-naphthylbutyric acid, m.p. 108—109°, cyclised (85% H₂SO₄) to 1-keto-1:2:3:4-tetrahydrophenanthrene-2:2-spirocyclopentane (I), b.p. 215°/6 mm. When reduced (Clemmensen), (I) gives 1:2:3:4-tetrahydrophenanthrene-2:2-spirocyclopentane, which with Se at 300—350° affords chrysene but no benzantracene. Similarly are obtained α -cyclopentyl- β -(4-methyl-1-naphthoyl)propionic acid, m.p. 176—177° and γ -(4-methyl-1-naphthyl)butyric acid, m.p. 112°, 1-keto-9-methyl-1:2:3:4-tetrahydrophenanthrene-2:2-spirocyclopentane, m.p. 97°, and 9-methyl-1:2:3:4-tetrahydrophenanthrene-2:2-spirocyclopentane, m.p. 69—70°, which with Se at 300—350° gives 6-methylchrysene, m.p. 152—153°. J. L. D.

Synthesis of picene. H. WALDMANN and G. PITSCHAK [with K. G. HINDENBURG] (Annalen, 1937, 527, 183—189).—K₂ *o*-phenylenediacetate (I), *o*-NO₂·C₆H₄·CHO, and Ac₂O at 80° and finally at 130—140° yield *o*-NO₂·C₆H₄·CH:CH·CO₂H and the isomeric forms of di-*o*-nitrobenzylideneindan-2-one, m.p. 241.5° and m.p. 199° (decomp.), respectively, also obtained from indan-2-one (II) and *o*-NO₂·C₆H₄·CHO in AcOH containing HCl. (I) and Ac₂O at 80—105° afford (II). Vigorous action between *o*-C₆H₄(CH₂·OH)₂, *o*-NO₂·C₆H₄·CHO, and 33% NaOH in EtOH leads to di-*o*-nitrobenzylidene-*o*-phenylenediacetonitrile, m.p. 228°, reduced by SnCl₂ in AcOH—conc. HCl to di-*o*-aminobenzylidene-*o*-phenylenediacetonitrile, m.p. 239—240°, which is converted by conc. H₂SO₄ at 80° into di-*o*-nitrobenzylidene-*o*-phenylenediacetamide, m.p. 241°, and thence by NaNO₂ and H₂SO₄ into di-*o*-nitrobenzylidene-*o*-phenylenediacetic acid, m.p. 291° [Na salt (III)]. (III) is reduced by Na₂S to di-*o*-aminobenzylidene-*o*-phenylenediacetic acid, m.p. 269° (decomp.) (Na salt), which is converted by NaNO₂, followed by Cu paste in H₂SO₄, into mainly a substance, m.p. 246°, containing N and picene-12:13-dicarboxylic acid (IV), m.p. (indef.) 320—324° (decomp.) [anhydride (V), m.p. 322—323°]. Ignition of (IV) with soda-lime yields picene, m.p. 356°. Sublimation of (V) at 330—340° gives unchanged material and 1:2:7:8-dibenz-4:5-phenanthrylene ketone (VI), m.p. 267°, transformed by distillation with Zn dust into 1:2:7:8-dibenz-4:5-phenanthrylenemethane, m.p. 277°. H. W.



into 1:2:7:8-dibenz-4:5-phenanthrylenemethane, m.p. 277°. H. W.

Preparation of methylcholanthrene. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1936, 58, 2482—2487).—The method previously described (A., 1935, 480, 853) is modified for relatively large-scale use. The mixture of ketones obtained from *p*-C₆H₄MeCl (I), CH₂Cl·CH₂·COCl (modified prep. of acid), and AlCl₃ in CS₂ is converted by conc. H₂SO₄ at 105—110° into a 2:1 mixture (A) of 4-chloro-7-methyl-, m.p. 82—82.4°, and 7-chloro-4-methyl-, m.p. 128°, -1-hydrindone (cf. Mayer and Müller, A., 1928, 65). Clemmensen reduction of (A) gives 7-chloro-4-methylhydrindene, b.p. 132—133°/25 mm., which with CuCN + C₆H₅N at 220—230° affords the 7-CN-derivative (II), m.p. 72.9—73.2°, hydrolysed (conc. HCl) to the amide, m.p. 176—177.4°, of 4-methylhydrindene-7-carboxylic acid, m.p. 227—229°. 7- α -Naphthoyl-4-methylhydrindene [from (II) and α -C₁₀H₇·MgBr] is pyrolysed at 405—410° (bath)/40 min. to methylcholanthrene (III) [over-all yield from (I) 20%] and some (probably) 7- α -naphthylmethyl-4-methylhydrindene, b.p. 221—226°/4 mm. The prep. of the choleic acid, m.p. 197.5—198°, from (III) and deoxycholic acid is detailed (cf. A., 1935, 1366).

The mixture of ketones obtained [as for (I)] from *p*-C₆H₄MeBr with conc. H₂SO₄ at 100° gives a little of (probably) a bromotolyl vinyl ketone, m.p. 129—132°, and much oil; bromomethylhydrindones could not be obtained by cyclisation. All m.p. are corr. H. B.

Identity of the dehydrogenation-hydrocarbons, C₂₅H₂₄, from cholesterol and ergosterol. O.

DIELS and H. J. STEPHAN (Annalen, 1937, 527, 279—290).—The identity of the hydrocarbons, $C_{25}H_{24}$ (best prepared by Se in boiling $NHPhAc$ and purified by crystallisation from $EtCO_2H$), from ergosterol (I) and cholesterol is confirmed by the m.p. (219—221°), mixed m.p., analysis, prep. of the $(NO_2)_2$ -compound, m.p. 262° (mixed m.p.), and oxidation to the ketone (II), $C_{25}H_{22}O$, identified by the m.p. 193—194°, mixed m.p., analysis, absorption spectrum, X-ray diagram, and crystallo-optical data (cf. Ruzicka *et al.*, A., 1934, 398). A NO_2 -compound is often formed as impurity in the $(NO_2)_2$ -compound. A higher-boiling hydrocarbon fraction from (I) with $Na_2Cr_2O_7$ - $AcOH$ gives also a yellow ketone, $C_{25}H_{22}O$ or $C_{26}H_{24}O$, m.p. 174—175°, which resembles (II) closely in absorption spectrum and with CrO_3 gives a substance, (?) $C_{25}H_{18}O_3$, m.p. 230—231° (not chrysoquinone).

R. S. C.

Separation of primary arylamines from secondary aralkylamines. C. W. FERRY and J. S. BUCK (J. Amer. Chem. Soc., 1936, 58, 2444—2445).—Mixtures of NH_2Ar (I) and $NHArAlk$ (II) are separated by treatment with aq. $PhCHO \cdot NaHSO_3$ [2 mols. calc. on (I) present], whereby the (II) does not react and is extracted with Et_2O . o - $C_6H_4Me \cdot NH_2$ can be separated from o - $C_6H_4Me \cdot NHEt$ by its preferential reaction with $PhNCO$. *N*-Phenyl-*N'*- α -naphthyl-*N*-methyl-, m.p. 99°, and -*n*-butyl-, m.p. 99°, *N*-*o*-, m.p. 85.5°, -*m*-, m.p. 95.5°, and -*p*-, m.p. 103°, -*tolyl*- and *N*-*o*-, m.p. 136.5°, and -*p*-, m.p. 111°, -phenetyl-*N'*- α -naphthyl-*N*-ethyl-, and *N*-*p*-anisyl-*N'*- α -naphthyl-*N*-isopropyl-, m.p. 147°, -*carbamides* are prepared from α - $C_{10}H_7 \cdot NCO$ and the appropriate (II). H. B.

Promoter action. Oxidation of aniline sulphate by hot concentrated sulphuric acid in presence of copper and mercury sulphates. M. M. HARING and H. H. KAVELER (J. Amer. Chem. Soc., 1936, 58, 2595—2599).—Destructive oxidation of $(NH_2Ph)_2 \cdot H_2SO_4$ by an excess of conc. H_2SO_4 at 275° is accelerated by $CuSO_4$ and $HgSO_4$ (better at higher concn.). The catalytic effect increases with rise in the concn. but is not directly \propto concn. as claimed by Bredig and Brown (A., 1904, ii, 247). Mixtures have activities $>$ the additive val.; the most active is an approx. 2 : 1 (mol.) mixture of $HgSO_4$ and $CuSO_4$. The reaction is unimol. or pseudounimol. in the first stages (cf. *loc. cit.*). H. B.

Complex compounds of 4-phenylselenosemicarbazide. K. A. JENSEN and E. FREDERIKSEN (Z. anorg. Chem., 1936, 230, 31—33).— $PhNCS$ with $N_2H_4 \cdot H_2O$ in $EtOH$ in the cold gives 4-phenylselenosemicarbazide, m.p. 157° (decomp.), which with $NiCl_2$ yields complex compounds, $[Ni(NHPh \cdot CSe \cdot NH \cdot NH_2)_2]Cl_2$ and $[Ni(NHPh \cdot CSe \cdot NH \cdot NH_2)_3]Cl_2$, the latter of which with $EtOH \cdot NH_3$ gives $Ni(NPh \cdot CSe \cdot NH \cdot NH_2)_2$.

F. L. U.

Electrolytic introduction of the thiocyanate group into aromatic amines and phenols. F. FICHTER and P. SCHÖNMANN (Helv. Chim. Acta, 1936, 19, 1411—1415).—Anodic electrolysis using a rotating graphite anode (cf. F.P. 702,829) of the base or phenol in aq. $EtOH \cdot HCl$ in presence of D (A., II.)

NH_4CNS (4 mols.) gives *p*-thiocyano-dimethyl- (91.7%) and -diethyl-aniline (68.9%), b.p. 138°/1 mm. (*picrate*, m.p. 134°), 3-thiocyano-*NN*-dimethyl-*p*-toluidine (21%), an oil (*hydrochloride*, cryst.), and 4-thiocyanoguaiacol ($OH = 1$) (prep. in aq. $EtOH$), m.p. 107° (also obtained in poor yield from 4-amino-guaiacol). R. S. C.

Nitration of benzyaniline and its derivatives.

II. P. VAN DEN BERG (Rec. trav. chim., 1936, 55, 1053—1067; cf. A., 1936, 1501).—*p'*-Nitrobenzyl-*p*-chloro-, m.p. 98° (*Ac* derivative, m.p. 102°), and -*bromo*-aniline, m.p. 119° (*Ac* derivative, m.p. 100°), and -*p*-toluidine (*Ac* derivative, m.p. 85°)-are nitrated (abs. HNO_3) to *p*-nitrobenzyl-4-chloro- (I), m.p. 186°, -*bromo*- (II), m.p. 145° and -methyl-2 : 6-dinitrophenyl-nitroamine (III), m.p. 186° which on further nitration (H_2SO_4 -abs. HNO_3) afford 2' : 4'-dinitrobenzyl-4-chloro-, m.p. 147°, -*bromo*-, m.p. 146°, and -methyl-2 : 6-dinitrophenyl-nitroamine, m.p. 144°, respectively. *o'*-Nitrobenzyl-*p*-chloro-, m.p. 112°, and -*bromo*-aniline, m.p. 87° (lit. 84—85°) [*Ac* derivative, m.p. 139° (lit. 137—138°)], and -*p*-toluidine on nitration (HNO_3 , *d* 1.46) yield *o*-nitrobenzyl-4-chloro- (IV), m.p. 139°, -*bromo*- (V), m.p. 160°, and -methyl-2 : 6-dinitrophenyl-nitroamine (VI), m.p. 158°, which give 2' : 4'-dinitrobenzyl-4-chloro-, m.p. 147°, -*bromo*-, m.p. 146°, and -methyl-2 : 6-dinitrophenyl-nitroamine, m.p. 144°, on further nitration (abs. HNO_3), whilst *m'*-nitrobenzyl-*p*-chloro-, m.p. 81° (*Ac* derivative, m.p. 120°), and -*bromo*-aniline, m.p. 72° (*Ac* derivative, m.p. 126°), -*p*-toluidine, m.p. 85° [identical with substance previously described as *p'*-tolyl-bis-(*m*-nitrobenzyl)amine] (*Ac* derivative, m.p. 101°), and -*p*-nitroaniline, m.p. 147° (*Ac* derivative, m.p. 212°), are nitrated (HNO_3 , *d* 1.46) to *m*-nitrobenzyl-4-chloro- (VII), m.p. 165°, -*bromo*- (VIII), m.p. 157°, and -methyl-2 : 6-dinitrophenyl-nitroamine (IX), m.p. 167°, and *m*-nitrobenzyl-2 : 4 : 6-trinitrophenyl-nitroamine (X), m.p. 149°. The original substituted anilines result from the condensation (30 min.; 120—140°) of the appropriate amine and nitrobenzyl chloride. (I), (IV), or (VII) affords 4-chloro-2 : 6-dinitrophenol, (II), (V), or (VIII) affords 4-bromo-2 : 6-dinitrophenol, whilst (III), (VI), or (IX) affords 2 : 6-dinitro-*p*-cresol and (X) affords picric acid on boiling with aq. Na_2CO_3 . F. N. W.

Application of Curtius degradation reaction to the synthesis of phenylethylamine. P. P. T. SAH and C. H. KAO (Sci. Rep. Nat. Tsing Hua Univ., 1936, 3, 525—532).—Application of the Curtius reaction to $CH_2Ph \cdot CH_2 \cdot CO_2H$ has given $CH_2Ph \cdot CH_2 \cdot NH_2$ [*styphnate*, m.p. 187—189° (decomp.)]; 3 : 5-dinitrobenzoate, m.p. 188—189°; 3 : 5-dinitro-*o*-toluate, m.p. 165—166°; β -phenylethylcarbamide, m.p. 115—116°. F. R. S.

Betaine-like complex salts. P. PFEIFFER [with H. BÖTTCHER, W. PRÄTORIUS, and L. M. KWAN] (Z. anorg. Chem., 1936, 230, 97—111; cf. A., 1933, 824).—The following are described: *Cu* dianiline benzene-, *p*-toluene-, and 1-naphthalene-sulphonates; *Cu* aniline-*o*-, -*m*-, -*p*-sulphonates (with $4H_2O$); *Na* H (+ $2H_2O$), *Ba* (+ $3H_2O$), and *Cu* (+ $2H_2O$) salts of α -naphthylamine-2 : 5-disulphonic acid; *Cu*

di-1:2-naphthylenediamine nitrate and sulphate; *Cu di-1:8-naphthylenediamine chloride, nitrate, and sulphate*; *Ni di-1:8-naphthylenediamine sulphate*; *Cu 1:2-naphthylenediamine-6-sulphonate*; *Cu and Ni 1:8-naphthylenediamine-4-sulphonate*; *Na (anhyd. and +3H₂O) and Ba salts of Cu di-1:8-naphthylenediamine-3:6-disulphonic acid*; *Cu di-4-α-naphthalene-azo-1:8-naphthylenediamine nitrate (+2H₂O)*. A dipolar structure similar to that of the betaines is attributed to the simpler Cu and Ni salts described.

F. L. U.

cis-trans-Isomeric stilbenes. IV. Stereoisomeric *o*-nitro- and *o*-amino-stilbenes, *o*-aminodibenzyl, and ring-closure to phenanthrene and dihydrophenanthrene. II. P. RUGGLI and A. STAUB [with, in part, O. SCHMID] (Helv. Chim. Acta, 1937, 20, 37—52).—The best yields (70%) of *cis-o*-nitrostilbene (I), m.p. 65—66°, b.p. 187°/11 mm., are obtained by addition of *o*-NO₂·C₆H₄·CH:CH·CO₂H to quinoline containing Cu chromite at 230°. (I) is not isomerised when distilled in a vac. or with superheated steam, or when boiled with HCl-H₂O-EtOH, and only slowly affected by insolation in C₆H₆ containing I. Partial isomerisation occurs at 230°, accelerated by I, but not in boiling quinoline or cymene. The most powerful reagent is PhNO₂ containing I at 210° whereas PhNO₂ alone has little effect. *trans-o*-Nitrostilbene has b.p. 209°/11 mm., m.p. 73°. (I) is not smoothly reduced by SnCl₂, whilst catalytic hydrogenation (Ni) leads to considerable amount of *o*-aminodibenzyl (II). Treatment with FeSO₄-NH₃ gives *cis-o*-aminostilbene (III), b.p. 180—181°/11 mm. (hydrochloride, m.p. 203°; sulphate, m.p. 159—161°; Ac, m.p. 114°, and Bz, m.p. 98°, derivatives; picrate, m.p. 145°), in 90% yield. Isomerisation of (III) occurs less readily than that of (I) and is best effected in quinoline at 250°. It occurs to some extent during the slow distillation of (III). Addition of I causes complete resinification, also observed when (III) is insolated in C₆H₆ containing I. *trans-o*-Aminostilbene (IV) gives an Ac derivative, m.p. 143°, a hydrochloride, m.p. 195—196°, sulphate, m.p. 204°, Bz derivative, m.p. 168°, and picrate, m.p. 156°. Diazotisation of (III) and treatment of the product with Cu paste affords phenanthrene in 61.3% yield, increased to 64% by the use of amyl nitrite in EtOH and to 80% when the diazo-product formed in EtOH is treated with NaHPO₂. On the other hand, (IV) gives no phenanthrene by this reaction; in H₂O much resin, some PhCHO, and *trans-o*-hydroxystilbene, m.p. 146—147° (acetate, m.p. 55—56°), are formed, whereas in EtOH with Cu powder stilbene is obtained in 62% yield. The difference in behaviour of the two stereoisomeric forms in the Pschorr reaction is due to spatial conditions, ring-closure being impossible with the *trans*-form. (II), m.p. 33°, gives a hydrochloride, m.p. 198°, sulphate, m.p. 202°, Ac, m.p. 117°, and Bz, m.p. 166°, derivative, and a picrate, m.p. 167—168°. The Pschorr reaction of (II) in H₂O or EtOH leads to *o*-hydroxydibenzyl, m.p. 85°, b.p. 171—172°/11 mm. (Ac derivative, b.p. 179°/11 mm.; 2':4'-dinitrophenyl ether, m.p. 69°), and 9:10-dihydrophenanthrene, b.p. 158°/11 mm., m.p. 34.5—35°, dehydrogenated by S at 210° to

phenanthrene and oxidised by CrO₃ in AcOH to phenanthraquinone; with NaH₂PO₂, Ph₂ is formed in 47% yield.

H. W.

Auxo-enoid systems. II. Colour of nitrobenzoyl derivatives of aromatic amines. III. Influence of the position of nitro- and auxo-groups on the colour of nitrobenzoylarylamides. V. A. ISMAILSKI and E. A. SMIRNOV (Bull. Soc. chim., 1937, [v], 4, 81—94, 94—111; cf. A., 1936, 1396).—II. The yellow to red colour of derivatives of the type NO₂·C₆H₄·Q·C₆H₄X (X = auxochrome OMe, OH, or NMe₂) is determined mainly by X and is of the same order if Q = ·CO·NH· instead of CH:CH, CH:N, or N:N so that conjugation between the NO₂- and auxo-group is broken. The colour of these compounds cannot be due to the structure ·C(OH)·N· since it is retained in derivatives containing ·CO·NR·, and even if either the NO₂- or the auxo-group is in a *m*-position. The theories of Burawoy (A., 1931, 144) and of Diltthey *et al.* (A., 1928, 627) are not acceptable and colour must be due to direct mutual action of isolated nitro-enoid and auxo-enoid systems. The following compounds, prepared by acylation of the appropriate NH₂-compound, are new: *m*-4-, m.p. 212°, and *m*-3-nitrobenzamido-, m.p. 219°, *p*-4-, m.p. 214°, and *p*-3-nitrobenzomethylamido-, m.p. 224°, -phenol; *p*-3-, m.p. 174.5°, and *p*-4-nitrobenzamidoanisole, m.p. 197°; *N*-3-, m.p. 176°, and *N*-4-nitrobenzoyl-N'N'-dimethyl-*m*-, m.p. 188°, and *N*-3-, m.p. 173°, and *N*-4-nitrobenzoyl-N'N'-dimethyl-*p*-, m.p. 258.5°, -phenylenediamine; *p*-3-, m.p. 224° (lit. m.p. 215—216°), and *p*-4-nitrobenzamidophenol, m.p. 263° (lit. m.p. 258°), are prepared.

III. The bathochromic effect of introduction of *m*- and *p*-NO₂ into the Bz and of *m*- or *p*-OH and NMe₂ into NHPh in NHBzPh (I) is studied by spectroscopic examination (curves plotted) of the above derivatives. A bathochromic effect is produced by introduction of a single auxochrome into (I) even in absence of NO₂, but is greatly increased by simultaneous NO₂-substitution. The bathochromic effects of *p*-NO₂ (58 mμ) and *p*-NMe₂ (64 mμ) are approx. equal and are greater in the *p*- than in the *m*-position, the complete series being (*p*-NO₂-*p*'-NMe₂) > (*m*-NO₂-*p*'-NMe₂) > (*p*-NO₂-*m*'-NMe₂) > (*m*-NO₂-*m*'-NMe₂). The two chromophoric systems NO₂·C₆H₄·CO (termed *aci*-chromophore rather than anti-auxochrome) and auxochrome (OH)NMe₂·C₆H₄·NH·CO· are largely independent, colour depending on the stronger chromophore, which may be either system, e.g., *p*-NO₂·C₆H₄·CO > *m*-OH·C₆H₄·NH, but *p*-NMe₂·C₆H₄·NH > *m*-NO₂·C₆H₄·CO. The effect of introducing a new chromophore depends mainly on the nature of the initial system, the weaker chromophore merely modifying the effect of the stronger. The group CO·NH merely modifies the condition of the two chromophores. The results are discussed on a polarity basis and Kaufmann's rule is amplified. The strongest chromophoric properties arise from the opposing polar (contra-inductive) effects of either *p*-di-auxo- or *p*-di-*aci*-chromophore groups, much weaker effects being produced by the *syn*-inductive system present in *m*-derivatives.

J. W. B.

Electrochemical properties of diphenylbenzidinesulphonic acid. L. A. SARVER and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1937, 59, 23—24).—Diphenylbenzidinedecasilphonic acid has been oxidised to the green and violet forms, and the subsequent reduction studied electrometrically. The green form is very stable, the violet less stable, and both are fairly sol. in H_2O and dil. acids. The titration curves show that the green product is a semiquinone. E. S. H.

Racemisation of some *d-o*-(2-dimethylamino-phenyl)phenyltrimethylammonium salts. D. E. COOK and E. E. TURNER (J.C.S., 1937, 88—89).—In aq. solutions of equimol. concn. at 90° the velocity of racemisation of *d-o*-(2-dimethylaminophenyl)-phenyltrimethylammonium salts is in the order *benzenesulphonate* (half-life period 210 min.) > iodide (I) (250 min.) > *d*-camphorsulphonate (II) (310 min.). There is no simple connexion between μ of the solvent and the velocity of racemisation, the half-life periods for (II) decreasing in the order $H_2O > EtOH > COMe_2 > MeCN > CHCl_3$. The activation energies for racemisation of (I) and (II) in H_2O are 11.5 and 19 kcal., respectively. J. W. B.

Azo-dyes. II. A. ROLLETT, R. BIRKNER, and K. R. POSSELT (Monatsh., 1936, 68, 403—406; cf. A., 1935, 1360).—Comparison is made of the colour of *o*-amino- and *o*-hydroxy-azo-dyes formed by coupling benzenoid diazo-components with 1:4- $NH_2 \cdot C_{10}H_6 \cdot SO_3H$ and 1:4- $OH \cdot C_{10}H_6 \cdot SO_3H$. *m*-Substituents (NH_2 , $NHAc$, SO_3H , NO_2) bring about little deepening of shade either in solution or dyeing; *o*-substituents deepen the shade in the order $NO_2, Cl > CO_2H > OMe > Me$. Methylation or acetylation of the dye 1:2:4- $NH_2 \cdot C_{10}H_5(N_2Ph) \cdot SO_3H$ deepens the shade but with 1:2:4- $NH_2 \cdot C_{10}H_5(N_2 \cdot C_6H_4 \cdot NO_2 \cdot p) \cdot SO_3H$ the reverse occurs. Methylation of the OH has little effect on the shade of dyes from 1:4- and 1:5- $OH \cdot C_{10}H_6 \cdot SO_3H$. The effect of *o*-, *m*-, or *p*-substituents in the benzene ring on the *p*-amino- and *p*-hydroxy-azo-dyes formed from 1:6- and 1:7- $OH \cdot C_{10}H_6 \cdot SO_3H$ and $NH_2 \cdot C_{10}H_6 \cdot SO_3H$ is < in the *o*-azo-series and in general the survey shows that groups which cause deepening of shade when *o* or *p* are without effect when *m* and *vice versa*. No spectroscopic measurements are given. K. H. S.

Action of hydrogen fluoride on phenyldiazomethane. C. L. TSENG, C. H. SZE, and C. E. SUN (J. Chinese Chem. Soc., 1936, 4, 485—489).— $CHPhN_2$ and abs. HF in Et_2O give a small amount of a substance containing 35.3% of F and much stilbene. Failure to obtain CH_2PhF is explained by thermal considerations: the activation energy for $CHPhN_2 + HF \rightarrow CH_2PhN_2F$ (I) is 105.5; (I) $\rightarrow CH_2PhF + N_2 + 124.8$, and $2CHPhN_2 \rightarrow (CHPh)_2 + 2N_2 + 10.8$ kcal. R. S. C.

Decomposition reactions of aromatic diazo-compounds. I. Evidence for non-ionic reaction. W. A. WATERS (J.C.S., 1937, 113—117).—The spontaneous decomp. of benzenesulphonic diazoacetate (prepared as $NPhAc \cdot NO$) into neutral Ph and OAc radicals and N_2 is indicated by the isolation of the products of further reaction with the solvent $Ph + RX \rightarrow PhX$ ($X = H$ or halogen). Thus in

$n-C_6H_{14}$, cyclohexane, Et_2O , dioxan, $COMe_2$, MeCN, $EtOAc$, and Ac_2O some C_6H_5 is formed; in RX and CHX_3 ($X =$ halogen) PhX is isolated, and $(PhS \cdot)_2$ is formed in CS_2 . In Ac_2O , CCl_4 , and CS_2 , CO_2 is liberated, indicative of the decomp. of free OAc radicals. In dry CS_2 , Fe, Zn, Cu, Pb, and Sb are attacked even in presence of $CaCO_3$ [gives some $Ca(OAc)_2$, showing formation of some $AcOH$], and in CCl_4 , Cu, Sn, Bi, and Hg (to give some $HgPhCl$) are attacked, diagnostic of free neutral OAc radicals. J. W. B.

Ethyl esters of tri-iodophenoxyacetic acids and potassium tri-iodophenoxyacetate. T. C. DANIELS and R. E. LYONS (J. Amer. Chem. Soc., 1936, 58, 2646).—*Et mono*-, m.p. 128.5°, *di*-, m.p. 160°, and *tri*-, amorphous, decomp. 208—211°. *Tri-iodophenoxyacetates* are prepared from $C_6H_2I_3 \cdot OH$ and *Et mono*-, *di*-, and *tri*-chloroacetate, respectively, in $EtOH-NaOEt$; the first only is hydrolysed by 30% aq. KOH to the acid, m.p. 211° (*K salt*).

Introduction of the chloromethyl group into *o*-nitroanisole and toluene. P. P. SCHORIGIN and S. A. SKOBLINSKAJA (J. Gen. Chem. Russ., 1936, 6, 1578—1582).—*o*-Nitroanisole and paraldehyde in light petroleum in presence of HCl and $ZnCl_2$ yield 3-nitro-4-methoxybenzyl chloride and 3:3'-dinitro-4:4'-dimethoxydiphenylmethane. $PhMe$ reacts similarly, to give *o*- and *p*-methylbenzyl chloride, whilst the reaction in the gaseous phase gives ditolylmethane as sole product. R. T.

Rearrangement of aryl allyl ethers. C. D. HURD and L. SCHMERLING (J. Amer. Chem. Soc., 1937, 59, 107—109).—In agreement with Claisen and Tietze (A., 1925, i, 389), *Ph cinnamyl ether* (I) (from $PhOH$, $CHPh \cdot CH \cdot CH_2Br$, and K_2CO_3 in $COMe_2$) heated in $NPhEt_2$ rearranges to *o*- α -phenylallylphenol (II) [phenylcarbamate, m.p. 93—94° (lit. 91°)]. The structures of (II) and *o*-cinnamylphenol (*loc. cit.*) are proved by ozonolysis. (I) heated with β - $C_{10}H_7$ allyl ether (III) at 240° (bath) gives (II) and 1-allyl-2-naphthol (IV); the non-formation of *o*-allylphenol indicates that rearrangement is not intermol. but is intramol. Similar evidence is obtained with (III) + *Ph hexenyl ether*; (IV) and *o*-hexenylphenol are isolable. *m*- $OH \cdot C_6H_4 \cdot ONa$ and α -bromo- Δ^8 -hexene in $EtOH$ give 4-hexenylresorcinol, *resorcinol hexenyl ether* (insol. in 10% $NaOH$), and some dihexenyl ether. The polymeric products formed when *Ph allyl ether* is heated at 210—240° (bath) are separable by distillation from a mol. still into a *dimeride* (probably 2- β -*o*-allylphenoxypropylphenol) and *trimeride* of *o*-allylphenol. H. B.

Fission of benzenesulphonic esters of pyrogallol. A. VON WACEK and I. SCHÖPFER (Österr. Chem.-Ztg., 1937, 40, 63—64).—Pyrogallol tribenzenesulphonate (I) is not hydrolysed by HBr , HI , or $HCl-EtOH$ at 170°; with liquid NH_3 at room temp., *pyrogallol 1:3-dibenzenesulphonate*, m.p. 127°, is formed [acetate, m.p. 137°; *Me ether* (by CH_2N_2), m.p. 109° (identical with product from $PhSO_2Cl$ and pyrogallol 2-Me ether)]. Boiling N_2H_4 causes complete fission of (I), giving pyrogallol (60%), Ph_2S_2 , and $PhSH$. J. D. R.

Pentenyl-, hexenyl-, and heptenyl-resorcinols. C. D. HURD and R. W. MCNAMEE (J. Amer. Chem. Soc., 1937, 59, 104—106).— m -C₆H₄(OH)₂ (I) and α -bromo- Δ^2 -hexene (II) in COMe₂ + anhyd. K₂CO₃ give *resorcinol dihexenyl ether* (III), 4-*hexenylresorcinol* (IV) (150; 200; 40) [Me₂ ether, b.p. 150—152°/10 mm., oxidised (KMnO₄, COMe₂) to 2:4-(OMe)₂C₆H₃·CO₂H; *di(carboxymethyl) ether*, m.p. 159—160°, prepared using CH₂Cl·CO₂H in 10% NaOH], and 4:6-*dihexenylresorcinol* (V) (>200; >200; >30) (Me₂ ether, b.p. 158—163°/10 mm.). (III)—(V) are also obtained from m -C₆H₄(ONa)₂ and (II) in C₆H₆; (V) is also formed from (I) and (II) in EtOH-NaOEt. Reduction (H₂, PtO₂, EtOH) of (IV) gives a product from which 4-*n*-hexylresorcinol is isolable. (I) and α -bromo- Δ^2 -pentene (VI) in COMe₂ + K₂CO₃ afford *resorcinol dipentenyl ether* and 4-*pentenylresorcinol* [Me₂ and *di(carboxymethyl)*, m.p. 164—165°, ethers], whilst α -bromo- Δ^2 -heptene (VII) gives 4-*heptenylresorcinol*, b.p. 138—143°/1 mm. [*di(carboxymethyl) ether*, m.p. 144—145°], and 4:6-*diheptenylresorcinol*. The above alkenyl derivatives are mixtures since (II), (VI), and (VII) are undoubtedly admixed with the γ -bromo- Δ^2 -alkene. Most of the compounds are purified by distillation from a Hickman mol. still. The nos. in parenthesis after (IV) and (V) are the PhOH-coeffs. towards *S. aureus*, *Strep. haemolyticus*, and *B. typhosus*, respectively.

H. B.

Catalytic dehydrogenation in the dibenzyl series. J. DEWAR and J. READ (J.C.S.I., 1936, 55, 347—349T).—Ordinary Pd- or Pt-C was found to be useless for the dehydrogenation of (CH₂Ph)₂ at 300°, but its dehydrogenation to phenanthrene (I) at this temp. in presence of Zelinski's Pt-C was confirmed (cf. A., 1927, 47; 1930, 80). The same catalyst dehydrogenated 4:4'-dimethoxydibenzyl (II) slowly, and since the OMe were detached simultaneously the product was again (I). An electrically heated vertical-tube furnace suitable for the above operations is described. Rupe's activated Ni catalyst was found to convert 4:4'-dimethoxystilbene partly into (II) in CO₂ atm. at 250°. Efficient methods are described for preparing (II), anisoin, hydroanisoin, isohydroanisoin, *hydroveratrin*, m.p. 210°, and *isohydroveratrin*, m.p. 167°, the last two in approx. equal, quant. yield by electrolytic reduction of veratraldehyde.

Nitration of 1:8-dihydroxynaphthalene. F. CALVET (Anal. Fis. Quím., 1936, 34, 650—666).—1:8-C₁₀H₆(OH)₂ could not be nitrated but nitration of 1:8-C₁₀H₆(OAc)₂ yields 2:4-dinitro-1-hydroxy-8-acetoxynaphthalene (I), m.p. 200° (decomp.), which cannot be acetylated or benzooylated. (I) with CH₂N₂ yields 2:4-dinitro-8-acetoxy-1-methoxynaphthalene (II), m.p. 115—117°, hydrolysed by cold aq. KOH to 2:4-dinitro-8-hydroxy-1-methoxynaphthalene, m.p. 170—171°. Boiling KOH-EtOH hydrolyses (I) and (II) to the (OH)₂-compound (III), m.p. 180—182° (decomp.), from which the (OMe)₂-compound (IV), m.p. 137—139°, is obtained, converted by KOH-EtOH into the 1-hydroxy-8-methoxy-compound (V), m.p. 179—180° (decomp.). (III) and (V) are reduced to *diamines* [hydrochlorides (VI) and (VII) isolated]. Oxidation of (VII) with boiling dil. HNO₃ gives

3-methoxyphthalic acid, establishing the structure of (III). Nitration of the methylene ether of 1:8-C₁₀H₆(OH)₂ yields the 2:7- (?) (VIII), m.p. 198—200°, and 4:5-, (IX), m.p. 177—179°, -(NO₂)₂-derivatives. Boiling aq. KOH converts (VIII) into the (OH)₂-compound (X), m.p. 171—173° (decomp.); KOH-EtOH gives the 1-hydroxy-8-methoxy-compound (XI), m.p. 218—220°. (X) and (XI) yield the (OMe)₂-compound, darkens 250°, m.p. 278° (decomp.). (X) yields Ac₁, m.p. 125—170° (decomp.), and Ac₂, derivatives, m.p. 228° (decomp.), and is reduced to the (NH₂)₂-compound [Bz₄ derivative, m.p. 300° (decomp.)]. Boiling aq. KOH hydrolyses (IX) to the (OH)₂-compound, m.p. 225° (decomp.) [Ac₂, m.p. 158—160°, and (OMe)₂-derivatives, m.p. 147—150° darkening and decomp.], which is reduced to the (NH₂)₂-compound, the Bz₄ derivative of which is identical with that obtained by the reduction and benzylation of 4:5-dibenzeneazo-1:8-dihydroxynaphthalene (Heller and Kretzschmann, A., 1921, i, 458). L. A. O'N.

Tetrahydroxybenzenes. F. MAUTNER (J. pr. Chem., 1937, [ii], 147, 287—292).—2:6-Dimethoxyphenol in EtOH is oxidised by HNO₃ (*d* 1.2) to 2:6-dimethoxy-*p*-benzoquinone (I), more conveniently obtained by similar treatment of pyrogallol Me₃ ether (prep. described). Reduction of (I) by Na₂S₂O₄ gives 2:6-dimethoxyquinol (II), m.p. 158°, the diacetate, m.p. 123°, of which is converted by AlCl₃ in PhNO₂ at 0° into 2:4-dihydroxy-4:6-dimethoxyphenyl Me ketone, m.p. 162—163°, which does not react with *p*-NO₂-C₆H₄-NH-NH₂ and is converted by AlCl₃ in boiling PhCl into 2:4:5:6-tetrahydroxyphenyl Me ketone, m.p. 243—244°. (II) and NaOH-Me₂SO₄ give 1:3:4:5-C₆H₂(OMe)₄, b.p. 271°, transformed by anhyd. Zn(CN)₂ and HCl in Et₂O followed by treatment of the product with warm H₂O into 2:4:5:6-tetramethoxybenzaldehyde, m.p. 88—89° (*p*-nitrophenylhydrazone, m.p. 178—179°). H. W.

Rearrangement of aryl alkyl sulphides. W. H. TAYLOR (J. Amer. Chem. Soc., 1936, 58, 2649—2650).—ArSalk undergo rearrangement and fission with AcOH-ZnCl₂ (Sprung and Wallis, A., 1934, 1097) at 135—150°. *p*-Tolyl alkyl sulphide thus gives 4-methyl-2-allylthiophenol, *p*-C₆H₄Me·SH, and allene; Ph sec-Bu sulphide, b.p. 104—105°/25 mm., affords sec-BuC₆H₄·SH, PhSH, and C₄H₈. *p*-Tolyl sec-Bu sulphide has b.p. 135—138°/22 mm. H. B.

Rearrangement of acetylenylcarbinols. C. D. HURD and R. E. CHRIST (J. Amer. Chem. Soc., 1937, 59, 118—121).—Contrary to Rupe *et al.* (A., 1928, 640), 1-acetylenylcyclohexanol is rearranged by HCO₂H to 1-acetyl- Δ^1 -cyclohexene (also prepared from cyclohexene, AcCl, and AlCl₃ in CS₂) and not to cyclohexylideneacetaldehyde (cf. Fischer and Löwenberg, A., 1929, 1421). CH₃C·CPhMe·OH similarly gives a little COPhMe [not CPhMe·CH·CHO (Rupe and Giesler, A., 1928, 870)] and much tar (probably arising from CH₂:CPh·COMe). Acetylenylbornyl alcohol, m.p. 97—98° (lit. 85°) (from camphor, Na, and C₂H₂ in C₆H₆), is rearranged by 90% HCO₂H to 6-hydroxy-2-acetylcamphane (I), m.p. 77—78°; the mechanism for the rearrangement involves two Wagner rearrangements. (I) is oxidised (O₃ in CCl₄)

to 6-hydroxycamphane-2-carboxylic acid, m.p. 221° (lit. 216—220°); the semicarbazone, m.p. 202°, prepared from (I) appears to be that of 1-acetylcamphene. The prep. of acetylenylfenchyl alcohol is improved (cf. Rupe and Kuenzy, A., 1931, 1068). H. B.

Tetrahydronaphthalene derivatives with basic side-chains. C. MANNICH, F. BARKOWSKY, and W. H. LIN (Arch. Pharm., 1937, 275, 54—62).—1-Ketotetrahydronaphthalene, 30% aq. CH_2O (1.1 mol.), and $\text{NHMe}_2\cdot\text{HCl}$ or piperidine hydrochloride (1.1 mol.), first at room temp. and then at 100°, give 70—75% yields of 1-keto-2-dimethylamino-, cryst. in ice-salt [hydrochloride, m.p. 144°; perchlorate, m.p. 121—123°; oxime (prep. in acid solution), an oil (hydrochloride, m.p. 188—189°)], and -piperidino-methyltetrahydronaphthalene, m.p. 37—38° [hydrochloride, decomp. 180°; oxime, m.p. 151° (hydrochloride, m.p. 198°)]. Reduction with 5% Na-Hg in dil. AcOH gives 1-hydroxy-2-dimethylaminomethyltetrahydronaphthalene, separable by way of the hydrobromides, m.p. 197° and 148°, respectively, into α - (I) (benzoate hydrochloride, m.p. 203°; p-nitrobenzoate hydrochloride, m.p. 189—190°) and β -forms (II) (benzoate hydrochloride, m.p. 171°; p-nitrobenzoate hydrochloride, m.p. 202°). 1-Hydroxy-2-piperidinomethyltetrahydronaphthalene, similarly prepared, gives the α - (III), m.p. 99—100° (hydrobromide, m.p. 180°; benzoate hydrochloride, m.p. 203°; p-nitrobenzoate hydrochloride, m.p. 185°), and β -forms (IV), b.p. 203—204°/14 mm. (hydrobromide, m.p. 193°; benzoate hydrochloride, m.p. 201°; p-nitrobenzoate hydrochloride, m.p. 191°; p-aminobenzoate, m.p. 142°). The isomerism of these alcohols is shown to be due to the newly formed asymmetric C_{10} , since both members of the pairs are dehydrated by an excess of HBr to yield the same 3-dimethylamino- (hydrobromide, m.p. 222°) and 3-piperidino-methyl-1:2-dihydronaphthalene (hydrobromide, m.p. 237°), hydrogenated (PtO_2) in AcOH to 2-dimethylamino- (hydrobromide, m.p. 180°) and 2-piperidino-methyltetrahydronaphthalene (hydrobromide, m.p. 231—232°). The benzoates of (I), (II), (III), and (IV) have 0.125, 0.5, 0.5, and 8 times, respectively, the local anæsthetic activity of cocaine, but are irritants. R. S. C.

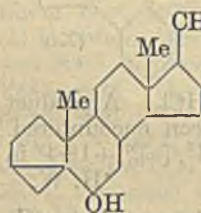
Synthesis of anisyl alcohol. A. OFNER (Helv. Chim. Acta, 1937, 20, 53—55; cf. A., 1935, 1120).—Contrary to Quelet (A., 1936, 1505), alkaline hydrolysis of $\text{OAc}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ affords $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ which is very readily dehydrated to $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2)_2\text{O}$ by technical Na_2SO_4 containing a trace of NaHSO_4 . H. W.

Deuterium abundance ratios in organic compounds. III. Cholesterol. M. DOLE and R. B. GIBNEY (J. Amer. Chem. Soc., 1936, 58, 2552—2555; cf. A., 1936, 667).—The D:H ratio in cholesterol is normal. On combustion there is marked fractionation of the O isotopes. E. S. H.

Molecular rearrangement in sterols. I. Action of anhydrous potassium acetate on cholesteryl p-toluenesulphonate in acetic anhydride solution. E. S. WALLIS, E. FERNHOLZ, and F. T. GEPHART (J. Amer. Chem. Soc., 1937, 59, 137—140; cf. Stoll, A., 1932, 737; Wagner-Jauregg and Werner, *ibid.*, 844; Benyon *et al.*, A., 1936, 1105).

Reaction between cholesteryl p-toluenesulphonate

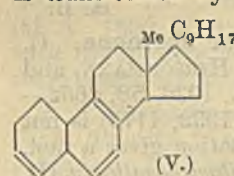
and anhyd. KOAc in Ac_2O at 70—80° is accompanied by a mol. rearrangement and gives the normal acetate together with about 43% of the acetate (I), m.p. 73°, $[\alpha]_D^{25} +47.8^\circ$ in CHCl_3 , of i-cholesterol (II), melts at room temp., resolidifying with m.p. 74—75°, $[\alpha]_D^{25} +23.9^\circ$ in CHCl_3 . (II) is considered not to contain a double linking since (I) does not react with BzO_2H and neither (I) nor (II) decolorises Br in CCl_4 . (II) is not pptd. by digitonin. (I) with H_2 and PtO_2 in AcOH gives dihydrocholesteryl acetate; reaction is slow with Pt-black and affords some cholestane. An impure ketone (oxime, $\text{C}_{27}\text{H}_{45}\text{ON}$, m.p. 143—144°) is obtained by oxidation (CrO_3 , AcOH) of (II). (II) and 3:5-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{COCl}$ in $\text{C}_5\text{H}_5\text{N}$ at 100° (bath



give 18% of cholesteryl 3:5-dinitrobenzoate, m.p. 193° (formed only in small amount at room temp.), whilst with AcOH-conc. H_2SO_4 at 100° some of the normal acetate is produced. The "abnormal" ethers of Stoll (*loc. cit.*) are probably related to (II), which may have the annexed structure. H. B.

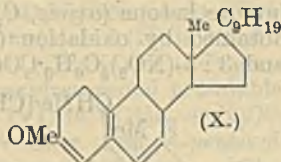
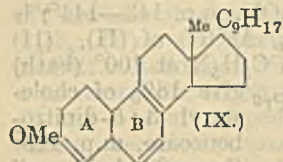
Photochemical dehydrogenation of 7-dehydrocholesterol. Y. URUSHIBARA and T. ANDO (Bull. Chem. Soc. Japan, 1936, 11, 802).—7-Dehydrocholesterol in EtOH in light in the presence of eosin gives a substance, $\text{C}_{54}\text{H}_{86}\text{O}_2$, m.p. 182—183° (corr.), possibly 7-dehydrocholestenopinacone. R. S. C.

Derivatives of neoergosterol. A. WINDAUS and M. DEPPE (Ber., 1937, 70, [B], 76—84).—Reduction of tetradehydronoergosterol (I) with Na and amyl alcohol gives epineoergosterol (II), m.p. 177°, $[\alpha]_D^{25} +27.4^\circ$ in CHCl_3 , which differs from the tetrahydrodehydrocholesterol of Marker *et al.* (A., 1936, 1256) since it cannot be removed from Et_2O by dil. or conc. KOH and does not resemble œstrone in absorption spectrum. Its constitution is proved by its formation from neoergosterol (III) and $\text{C}_5\text{H}_{11}\cdot\text{ONa}$ in boiling amyl alcohol. It gives an acetate (II), m.p. 98°, $[\alpha]_D^{25} +27.2^\circ$ in CHCl_3 , and dinitrobenzoate, m.p. 204°, $[\alpha]_D^{25} +21.2^\circ$ in CHCl_3 , from which it is regenerated by hydrolysis with KOH-MeOH. Further, (II) or (III) is transformed by $\text{NaOEt}\cdot\text{EtOH}$ at 200° into ergopentaene (V), m.p. 89—90°, $[\alpha]_D^{25} +69.5^\circ$ in EtOH. Tetradehydronoergosteryl acetate is hydrogenated (Pt-black in $\text{EtOAc}\cdot\text{Et}_2\text{O}$) to tetradehydrodihydronoergosteryl acetate (VI), m.p. 144°, $[\alpha]_D^{25} +32.4^\circ$ in CHCl_3 , hydro-



lysed to tetradehydrodihydronoergosterol, m.p. 140°, also obtained by dehydrogenation of dihydronoergosterol by Pt. Reduction of (VI) with Na and PrOH yields dihydroepineoergosterol (VII), m.p. 167°, $[\alpha]_D^{25} +28.8^\circ$ in CHCl_3 , the acetate, m.p. 83°, $[\alpha]_D^{25} +24.6^\circ$ in CHCl_3 , of which is also obtained by hydrogenation (Pt-sponge in Et_2O) of (IV). In further attempts to prepare by direct hydrogenation a substance with aromatic ring A, tetradehydronoergosteryl Me ether (VIII) is converted by Na and PrOH into 3:4-de

hydroneoergosteryl Me ether (IX), m.p. 151°, $[\alpha]_D^{25} +35.6^\circ$ in CHCl_3 , the structure of which is established by its conversion into (VII) by H_2 in presence of Pt; ring B therefore remains unaffected. If (VIII) is cautiously hydrogenated (Pt-sponge) the double linking in the side-chain is attacked, with formation of *tetradehydrodihydroneoergosteryl Me ether*, m.p. 108°, $[\alpha]_D^{25} +31.5^\circ$ in CHCl_3 , also obtained by dehydrogenation (Pt) and subsequent methylation of dehydroneoergosterol and transformed by Na and amyl alcohol into *dihydro-3:4-dehydroneoergosteryl Me*

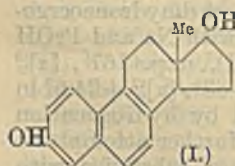


ether (X), m.p. 93°, $[\alpha]_D^{25} +30.2$ in CHCl_3 . A product with unchanged ring A has not been encountered. *epiNeoergosteryl Me ether* has m.p. 74°, $[\alpha]_D^{25} +18.4^\circ$ in CHCl_3 . H. W.

Antirachitic substance from tunny-liver oil. E. J. H. SIMONS and T. F. ZUCKER (J. Amer. Chem. Soc., 1936, 58, 2655).—The EtOH-sol. fraction of the unsaponifiable matter is freed from hydrocarbons and cholesterol; an alcohol (I) is then isolated through its 3:5-dinitrobenzoate, m.p. 128.5°. (I) has antirachitic activity of 30×10^6 I.U., shows absorption at 265 mμ, and is probably identical with the substance isolated by Brockman (A., 1936, 1161; cf. Haslewood and Drummond, *ibid.*, 1161). H. B.

α-Sitosterol. E. S. WALLIS and E. FERNHOLZ (J. Amer. Chem. Soc., 1936, 58, 2446—2448).—Crude "α-sitosterol" (Anderson *et al.*, B., 1927, 48, 49) with $\text{BzCl}-\text{C}_5\text{H}_5\text{N}$ gives (mainly) β-sitosteryl benzoate. Hydrolysis of the more sol. ($\text{EtOH}-\text{C}_6\text{H}_6$) fraction and subsequent 3:5-dinitrobenzoylation ($\text{C}_5\text{H}_5\text{N}$) affords small amounts of α₁-sitosterol (I), $\text{C}_{29}\text{H}_{48}\text{O}$, m.p. 164—166°, $[\alpha]_D^{25} -1.7^\circ$ in CHCl_3 [as 3:5-dinitrobenzoate, m.p. 222°, oxidised (BzO_2H in CHCl_3) to a dioxide, m.p. 209—212°; acetate, m.p. 137°; benzoate, m.p. 168—172°], and α₂-sitosterol (II), probably $\text{C}_{30}\text{H}_{50}\text{O}$, m.p. 156°, $[\alpha]_D^{25} +3.5^\circ$ in CHCl_3 [as 3:5-dinitrobenzoate, m.p. 206°; acetate, m.p. 124—126°; benzoate, m.p. 164—166°]. (I) and (II) both contain two double linkings. (I) is isomeric with stigmasteryl; both are pptd. by digitonin. H. B.

Chemical nature of δ-follicular hormone. O. WINTERSTEINER, E. SCHWENK, H. HIRSCHMANN, and B. WHITMAN (J. Amer. Chem. Soc., 1936, 58, 2652—2653).—δ-Follicular hormone (A., 1932, 1173) is not homogeneous; fractional crystallisation gives a mol. compound, m.p. 226° (corr.), of *dihydroequilenin* (I), m.p. 215—217°, $[\alpha]_D^{25} -4.7^\circ$ in dioxan [di-*p*-nitrobenzoate, m.p. 250—252° (corr.); benzoate, m.p. 203—205° (corr.)], oxidised (CrO_3) to the benzoate of equilenin (II)], and an unidentified substance, which, unlike (I), does not form a picrate. The absorption spectrum of (I) coincides with that of (II). (II) is twice as oestrogenic as (I). H. B.



Reduction of cholic acids by Bouveault's method. M. VANGHELOVICI (Bul. Soc. Chim. România, 1936, 18, 103—106).—Et cholate and Na-EtOH give 2—3% of the alcohol, $\text{C}_{24}\text{H}_{42}\text{O}_4$, m.p. 227°, which has a tonic action on the snail's heart. Et deoxycholate and cholinate give (no details) alcohols, m.p. 150° and 105°, respectively, which are difficult to purify. R. S. C.

Vegetable heart poisons. XII. Stereochemistry of the aglucons of the heart poisons. R. TSCHESCHE and K. BOHLE (Ber., 1936, 69, [B], 2443—2446).—A general review, provoked by the very slight physiological activity of azarin, leads to the conclusion that in all the highly active and thoroughly investigated heart poisons of the digitalis group the *cis*-union of rings A and B is maintained. A mechanism is suggested for the isomerisation of strophanthidin derivatives from the α- to the β-series. H. W.

Ethyl imidocyclopropanecarboxylate [α-imino-α-cyclopropylmethyl ethyl ether] hydrochlorides. J. B. CLOKE, E. C. KNOWLES, and R. J. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 2547—2549).—α-Imino-α-cyclopropyl- (I), α-1-phenyl-1-cyclopropyl- (II), m.p. about 110° (some decomp.), and α-1-phenyl-2-methylcyclopropyl- (III) methyl Et ether hydrochlorides are prepared from the appropriate cyanocyclopropane, EtOH, and HCl in (usually) Et_2O . Pyrolysis of (I) and (II) gives cyclopropanecarboxylamide, m.p. 120° (lit. 124—124.5°), and 1-phenylcyclopropane-1-carboxylamide, respectively; pyrrolinium salts are not produced (cf. A., 1929, 703). The rates of reaction of (I)—(III) with H_2O are determined by Derby's method (A., 1908, i, 419); comparison with results for other imino-ether hydrochlorides (cf. Stieglitz, A., 1908, ii, 167) classifies cyclopropyl with the electronegative aryl radicals. H. B.

Mechanism of amination by means of sodamide. II. Preparation of unsubstituted aromatic amidines by the action of sodamide on nitriles. A. V. KIRSANOV and I. M. POLJAKOVA (J. Gen. Chem. Russ., 1936, 6, 1715—1720).—PhCN and NaNH_2 in PhMe (6 hr. at the b.p.) give benzamidine; the reaction also proceeds very slowly at room temp. Toluamidine (picrate, decomp. at 219°; salicylate, m.p. 210—211°) and naphthamidine were obtained analogously from *p*-tolunitrile and α- $\text{C}_{10}\text{H}_7\text{CN}$. The reaction is represented as $\text{RCN} + \text{NaNH}_2 \rightarrow \text{NH}_2\cdot\text{CR}:\text{NNa} \rightarrow \text{NH}_2\cdot\text{CR}:\text{NH}$. R. T.

Removal of HX from organic compounds by means of bases. III. Rates of removal of hydrogen bromide from substituted *N*-bromobenzamides and their relative ease of rearrangement in presence of alkali. Hofmann rearrangement. C. R. HAUSER and W. B. RENFROW, jun. (J. Amer. Chem. Soc., 1937, 59, 121—125).—The rates of decomp. of various *N*-bromobenzamides by a large excess of NaOH at 30° are determined by the rate of disappearance of the active Br. For the *m*- and *p*-derivatives studied, the relative rates are inversely related to the dissociation consts. of the corresponding benzoic acids, indicating that the ease of the change $\text{RCO}\cdot\text{NHBr} \rightarrow \text{RNCO}$ is dependent on the ease of release of Br^- from $\text{RCO}\cdot\text{NBr}^-$. The yield

of the final product, *i.e.*, amine, is usually >90%; the yield from the *p*-NO₂-derivative is increased from 48 to 90% by carrying out the reaction at 96–100°. The following C₆H₄R·CO·NHBr, prepared by a modification of Hoogewerff and van Dorp's method (A., 1889, 981), were investigated: *N*-bromo-*p*-methyl-, decomp. 131–133°, -*o*-, decomp. 104–105°, -*m*-, decomp. 103–105°, and -*p*-, decomp. 170–174°, -chloro-, -*m*-bromo-, decomp. 122–126°, and -*o*-, decomp. 170–176°, -*m*-, decomp. 173–176°, and -*p*-nitro-, decomp. 198–202°, benzamides. H. B.

Steric hindrance. I. Non-saturation index in the cinnamic series. M. P. DUGUENOIS (Bull. Soc. chim., 1937, [v], 4, 193–199).—Theoretical addition occurs in 2 hr. in the dark when Br is added to CHPh·CH₂ or CHPh·CH·CO₂H at –10° in Et₂O (Volmar *et al.*, B., 1928, 236). Under such conditions addition of Br to CHPh·CH·CHO or CHPh·CH·CO₂H is incomplete but is complete in 2 hr. in diffuse sunlight. J. W. B.

Synthesis of β-1-phenanthrylpropionic acid. S. NATELSON and S. P. GOTTFRIED (J. Amer. Chem. Soc., 1937, 59, 216).—Phenanthrene-1-aldehyde, CH₂(CO₂H)₂ (excess), and a little C₆H₅N at 100° (bath) give β-1-phenanthrylacrylic acid, m.p. 259°, reduced (3% Na–Hg, dil. KOH) to β-1-phenanthrylpropionic acid, m.p. 187–188°. H. B.

Condensation of chloral with salicylic acid. F. CALVET and M. N. MEJUTO (Anal. Fis. Quim., 1936, 34, 641–649).—Condensation of CCl₃·CHO with *o*-OH·C₆H₄·CO₂H (I) by means of conc. H₂SO₄ yields firstly 2-hydroxy-5-ββ-trichloro-α-hydroxyethylbenzoic acid (II), m.p. 180–182°, and then 4:4'-dihydroxy-diphenyltrichloromethylmethane-3:3'-dicarboxylic acid (III), also obtained from (I) and (II). (II) yields an Ac₂ derivative, m.p. 190–192°, and Me ester, m.p. 97–99° (Ac₂ derivative, m.p. 90–92°). (II) with H₂SO₄ or KOH–MeOH yields 5-formyl-2-hydroxybenzoic acid, oxidised to 4-hydroxyisophthalic acid (IV). (II) on oxidation yields (IV) and on reduction a substance, C₉H₅O₃Cl₂, m.p. 170–172°, probably 2-hydroxy-5-ββ-dichlorovinylbenzoic acid. (III) yields a Me₂ ester, m.p. 200–202° (Ac₂ derivative, m.p. 207–209°), hydrolysed to ββ-dichloro-αα-4:4'-dihydroxydiphenylethylene-3:3'-dicarboxylic acid, m.p. 295–297° (Me₂ ester, m.p. 120–122°). L. A. O'N.

Electrolysis of aromatic carboxylic acids. III. Benzaldehyde-2-carboxylic acid. V. M. RODIONOV and V. V. LEVTSCHENKO (J. Gen. Chem. Russ., 1936, 6, 1563–1566).—Electrolysis of aq. 1:2-CHO·C₆H₄·CO₂K yields phthalide, α- and β-hydrodiphtalyl, and phthalic acid. R. T.

Condensation of ethyl dichloroacetate with ketones and aldehydes by very dilute amalgams. G. DARZENS (Compt. rend., 1936, 203, 1374–1376; cf. A., 1911, i, 6).—CHX₂·CO₂Et (X = Cl or Br) with COPhMe in dry Et₂O containing Mg-, Ca-, or Zn–Hg (1 in 50) affords Et α-chloro-β-hydroxy-β-phenylbutyrate in >90% yield. The reaction is of general application to ketones or aldehydes. J. L. D.

Degradation of *p*-hydroxydiphenylacetic acid to *p*-hydroxybenzhydramine. A. DARAPSKY and H. BERGER (J. pr. Chem., 1936, [ii], 147, 161–

166).—Et *p*-hydroxydiphenylacetate when refluxed with N₂H₄·H₂O–EtOH gives *p*-hydroxydiphenylacet-hydrazide, m.p. 194–197° (decomp.), which with HNO₂ gives the corresponding, unstable azide (I), and, unlike the corresponding *o*-compound (this vol., 85), is stable to cold conc. HCl and to boiling dil. HCl. (I) when boiled in C₆H₆ gives N₂, *s*-bis-*p*-hydroxybenzhydramine, m.p. 215°, and *p*-hydroxybenzhydramine (II), m.p. 113° [hydrochloride, m.p. 180° (decomp.)]; perchlorate, m.p. 96°. (I) when boiled with EtOH gives Et *p*-hydroxybenzhydramine, m.p. 55° (decomp.), hydrolysed by NaOH to (II). H. G. M.

Phthalyl chloride. L. P. KYRIDES (J. Amer. Chem. Soc., 1937, 59, 206–208).—Phthalyl chloride (I) is obtained in good yield from *o*-C₆H₄(CO)₂O (II) and SOCl₂ in presence of a little anhyd. ZnCl₂ at 220°. Passage of SO₂ through (I) + ZnCl₂ at 200° gives SOCl₂ and (II). (I) is also formed from (II) and CPhCl₃ + ZnCl₂ (larger amount) at 110–120°. (I) converts PrCO₂H and maleic anhydride (presence of ZnCl₂ essential) at 140° into PrCOCl and fumaryl chloride, respectively. H. B.

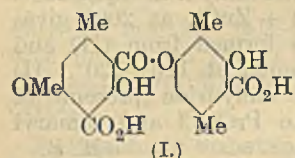
Condensations by sodium. VIII. Solvent exchange reactions, preparation of phenylmalonic acid, and mechanisms of reactions which employ sodium. A. A. MORTON and I. HECHENBLEIKNER (J. Amer. Chem. Soc., 1936, 58, 2599–2605).—*n*-Amyl chloride (I) and Na powder in C₆H₆ or C₆H₆–light petroleum followed by CO₂ give (according to conditions used) BzOH (11.5–78%), *m*- + *p*-C₆H₄(CO₂H)₂ (II) (0–6.5%), and CHBu(CO₂H)₂ (III) (trace–17.5%); use of PrCl and (CH₂)₂O in place of CO₂ affords PhPr and CH₂Ph·CH₂·OH, respectively. In the above reactions NaPh is produced. (I) and Na with PhMe, NPhMe₂, PhOMe, CH₂Ph₂, and fluorene in light petroleum followed by CO₂ give varying amounts of CH₂Ph·CO₂H (IV) [accompanied by CHPh(CO₂H)₂ (V)], *o*-NMe₂·C₆H₄·CO₂H, *o*-OMe·C₆H₄·CO₂H, CHPh₂·CO₂H, and fluorene-9-carboxylic acid, respectively. (IV) and (V) are also formed when Bu²Cl is used instead of (I). Evidence supporting the following reactions is discussed: (i) C₅H₁₁Na + C₆H₆ → C₅H₁₂ + NaPh; (ii) C₅H₁₀·(radical) + C₆H₆ → C₅H₁₂ + C₆H₅· [whence C₆H₄Na₂ → (II)] or C₅H₁₀Na₂ + C₆H₆ → C₅H₁₂ + C₆H₄Na₂; (iii) 2C₅H₁₁ → C₅H₁₂ + C₅H₁₀ [whence C₅H₁₀Na₂ → (III)]. The Wurtz–Fittig reaction is considered (cf. A., 1936, 1359) to proceed by reaction of NaAlk with AlkCl; free Alk radicals are present during the early stages and these react with Na. H. B.

2:2'-Derivatives of diphenyl. D. E. COOK and E. E. TURNER (J.C.S., 1937, 117–118).—Diphenoyl chloride and excess of MgMeI give a mixture of 2:2'-di-α-hydroxyisopropylidiphenyl (I), m.p. 138–139° (more sol. in ligroin), and 2-acetyl-2'-α-hydroxyisopropylidiphenyl (II), m.p. 164–165° (less sol.). (I) is also obtained from MgMeI and 2:2'-diacetyldiphenyl (III), m.p. 94–95° (lit. m.p. 84°), Me diphenate, or (II). Dehydration of (I) with PBr₃ at 90–100° gives 2:2'-di-α-methylvinylidiphenyl, m.p. 97–98°: replacement of OH by halogen could not be effected. (III) with Br–AcOH gives a substance, C₂₄H₁₈O₃Br₄, m.p. 134–135°. J. W. B.

Anthracene-1:2-dicarboxylic anhydride. O. BENNDORF (Monatsh., 1936, 69, 420—423).—Reduction of anthraquinone-1:2-dicarboxylic acid with Zn dust and boiling dil. NH_3 and dehydration of the product with boiling Ac_2O gives *anthracene-1:2-dicarboxylic anhydride* (I), m.p. 236°. (I) suspended in C_6H_6 is transformed by MgPhBr in Et_2O into 1- α -hydroxybenzhydrylanthracene-2-carboxylactone, m.p. 199°, with smaller amounts of 1-benzoylanthracene-2-carboxylic acid, m.p. 239° (Na salt), oxidised to 1-benzoylanthraquinone-2-carboxylic acid, m.p. 302°.

H. W.

Lichen substances. LXXII. Constitution of squamatic acid. Y. ASAHINA and Y. TANASE. **LXXIII. Synthesis of dimethyl squamate.** Y. ASAHINA and Y. SAKURAI (Ber., 1937, 70, [B], 62—63, 64—66).—LXXII. Extraction of the thalli of



Cladonia bellidiflora with Et_2O followed by COMe_2 gives *l-usnic acid* and *squamatic acid* (I), m.p. 219° (decomp.) [Me_2 ester (II), m.p. 178°]. The Me_2 ester

Me_2 ether of (I) is converted by boiling 95% HCO_2H into *Me 2:6-dimethoxy-3-carboxy-p-toluate* and *Me 4:6-dihydroxy-2:5-dimethylbenzoate*, thus confirming the annexed structure for (I).

LXXIII. *p*-Orsellinic acid is converted by CH_3N_2 into the *Me* ester, m.p. 98°, which with anhyd. HCN , HCl , and AlCl_3 in abs. Et_2O followed by treatment with boiling H_2O gives *Me 2:6-dihydroxy-3-aldehyde-p-toluate*, m.p. 146° (corresponding *anil*, m.p. 138°), transformed by Ag_2CO_3 and MeI in boiling COMe_2 into the corresponding *Me*, (III), m.p. 135°, and *Me*, m.p. 95.5°, *ethers*. (III) with ClCO_2Et and $\text{C}_5\text{H}_5\text{N}$ at room temp. affords the *carbethoxy-derivative*, m.p. 132.5°, oxidised by KMnO_4 in COMe_2 to *Me 6-methoxy-2-carbethoxy-3-carboxy-p-toluate* (IV), m.p. 127.5. (IV) is transformed by SOCl_2 , coupling of the chloride with *Me* β -orcinolcarboxylate, and subsequent decarboxylation into (II), identical with that derived from natural (I).

H. W.

Mellitic acid from coals, cokes, and graphites. B. JUETTNER (J. Amer. Chem. Soc., 1937, 59, 208—213).—Mellitic acid (I) is best obtained from various carbonaceous materials by successive oxidation with HNO_3 (*d* 1.5) (containing a little NH_4 vanadate) and alkaline KMnO_4 (excess). The g. of (I) from 100 g. of the following are quoted in parentheses: Edenborn coal (5.5), Edenborn coke prepared at 500°, 540°, 700°, and 1000° (11.9, 15.5, 24.1, and 22.5, respectively), Acheson electrode graphite (19.1), micronised Dixon graphite (natural) (21.7), "Aquadag" (dry material) (8.3). (I) is isolated from the aq. solution by electro-dialysis and conversion into the NH_4 salt. H. B.

Preparation of benzaldehyde from benzylidene chloride and boric acid. J. MAKAROV-SEMLIANSKI and S. PROKIN [with V. IVANOVA and B. IVANOV] (J. pr. Chem., 1937, (ii), 147, 317—320).— CHPhCl_2 and H_3BO_3 at 130—160° afford PhCHO in 85% yield. Similar treatment of a fraction obtained by chlorinating boiling PhMe gives PhCHO , CH_2PhCl , and BzOH . CH_2PhCl does not react with H_3BO_3 .

PhCHO and H_3BO_3 at 130—140° do not appear to yield the compound $\text{CHPh} \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{B} \cdot \text{OH}$, the solid products being HBO_2 and $\text{H}_2\text{B}_4\text{O}_7$. H_3BO_3 can be regenerated without loss and pure HCl is evolved.

H. W.

Reducing action of potassium and sodium benzyloxide on aldehydes. L. PALFRAY, S. SABETAY, and P. MASTAGLI (Compt. rend., 1936, 203, 1523—1525).—Cuminaldehyde with boiling 0.5*N*- $\text{CH}_2\text{Ph} \cdot \text{OK}$ affords BzOH and cumyl alcohol. Heptaldehyde with 0.5*N*- $\text{CH}_2\text{Ph} \cdot \text{ONa}$ (I) affords BzOH (0.5 mol. per 1 mol. aldehyde), and β -*n*-amyl-*n*-nonyl alcohol (A., 1934, 1334) [*allophanate*, m.p. 120° (block)], identical with the synthetic product, together with some α -amylcinnamyl alcohol and its H_2 -derivative. The amount of BzOH formed is sufficient to prove the hydrogenating action of (I) on the product of the aldol condensation. Similarly (I) converts α -amylcinnamaldehyde into α -amylidihydrocinnamyl alcohol.

J. L. D.

Reaction of acinitro-derivatives with halogen compounds. V. Reaction of potassio-9-*acinitrofluorene* with halogeno-ketone derivatives. D. A. ISĂCESCU (Bul. Soc. Chim. România, 1936, 18, 63—65; cf. A., 1930, 1569).—The K salt of 9-*acinitrofluorene* with $\text{COMe} \cdot \text{CH}_2\text{Br}$ or $\text{COPh} \cdot \text{CH}_2\text{Br}$ in hot 96% EtOH gives 97 and 84% yields of aq. solutions of AcCHO and BzCHO , respectively.

R. S. C.

Iodination of 3-hydroxy- and of nitrated 3-hydroxy-benzaldehydes, and nitration of certain iodo-3-hydroxybenzaldehydes. H. H. HODGSON and E. W. SMITH (J.C.S., 1937, 76—78).—*m*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ when warmed with I-aq. NaOAc gives its 6-*I*-derivative, m.p. 130° (*p*-nitrophenylhydrazone, m.p. 215°); with I-aq. Na_2CO_3 the 2:6- I_2 -derivative (I), m.p. 144° (*Me* ether, m.p. 81°), and the 2:4:6- I_3 -derivative, m.p. 146° [*Na* salt; *Me* ether, m.p. 162°; *p*-nitrophenylhydrazone, m.p. 237° (decomp.)], are obtained after liberation from their Na salts with CO_2 . 2-Nitro-3-hydroxybenzaldehyde (improved prep.) [*p*-nitrophenylhydrazone, m.p. 250° (decomp.)] with aq. I gives its 4:6- I_2 -derivative, m.p. 158° (II) (lit. m.p. 154.5°) [*p*-nitrophenylhydrazone, m.p. 250° (decomp.)]; 6-nitro-3-hydroxybenzaldehyde with I- CHCl_3 - HgO gives its 2:4- I_2 -derivative [*p*-nitrophenylhydrazone, m.p. 244° (decomp.); *Me* ether, m.p. 142° [*p*-nitrophenylhydrazone, m.p. 220° (decomp.)]]. 2:6-Dinitro-3-hydroxybenzaldehyde with I-20% NaOH affords its 4-*I*-derivative, m.p. 168° (*p*-nitrophenylhydrazone, decomp. 310°), and the corresponding 4:6-(NO_2)₂-compound gives its 2-*I*-derivative, m.p. 106.5° [*p*-nitrophenylhydrazone, m.p. 282° (decomp.)]. HNO_3 (30%) converts (I) into its 4- NO_2 -derivative [*Na* salt; *p*-nitrophenylhydrazone, m.p. 218° (decomp.)], whereas HNO_3 (*d* 1.5) converts (II) into 6-iodo-2:4-dinitro-3-hydroxybenzaldehyde, m.p. 160°. 4-Nitro-3-hydroxybenzaldehyde is oxidised only to the acid by I-KI- Na_2CO_3 . J. W. B.

Synthesis of vanillin by Mottern's method. P. P. SCHORIGIN and K. I. BOGATSHEVA (J. Gen. Chem. Russ., 1936, 6, 1567—1568).—Attempts at repeating Mottern's synthesis (A., 1934, 1354) were unsuccessful.

R. T.

Derivatives of cyclopentanone. M. C. CHANG and P. P. T. SAH (J. Chinese Chem. Soc., 1936, 4, 413—417).—The following derivatives of cyclopentanone are prepared: *phenyl*-, m.p. 164—165°, p-, m.p. 180—181°, *o*-, m.p. 165—166°, and *m-tolyl*-, m.p. 192—193°, α -, m.p. 183—184°, and β -*naphthyl-semicarbazone*-, m.p. 179—180°; p-, m.p. 173—174°, *o*-, m.p. 203—204°, and *m-nitro*-, m.p. 143—144°, 3:5-dinitro-, m.p. 212—214°, and *m-bromo-benzoyl-hydrazone*-, m.p. 164—165°. M.p. are corr.

R. S. C.

Aldehydes and hydroxyaldehydes of the polymethylenic series. II. Condensation products of cyclopentanone. E. D. VENUS-DANILOVA (J. Gen. Chem. Russ., 1936, 6, 917—921; cf. A., 1936, 1109).—MgBu²Cl and cyclopentanone in boiling Et₂O yield a small quantity of cyclopentanol and more 1-cyclopentylidenecyclopentan-2-one (I), b.p. 122—123°/16 mm. [*semicarbazone*-, m.p. 214° (decomp.)]. Hydrogenation of (I) in presence of Pt leads to 1-cyclopentylcyclopentan-2-one (II) (*oxime*-, m.p. 78°; *semicarbazone*-, m.p. 209—210°). cyclopentanone and Na in H₂O + Et₂O without EtOH give a small quantity of 1:1'-dihydroxydicyclopentyl and more cyclopentanol and 1-cyclopentylcyclopentan-2-ol, b.p. 119—120°/14 mm. (*acetate*-, b.p. 121—122°/10 mm.), which is oxidised by CrO₃ to (II).

J. J. B.

Catalytic hydrogenation of alicyclic ketazines. Hydrogenation of cyclohexanone ketazine and its methyl derivatives. V. I. EGOROVA (J. Gen. Chem. Russ., 1936, 6, 1404—1417).—The velocity of hydrogenation of ketazines of cyclohexanone (I) and its Me derivatives (in AcOH or EtOH; Pt catalyst) falls in the order (I) > 4- > 3- > 2-methylcyclohexanone ketazine. The ketazines of (I) and 4-, b.p. 175—177°/23 mm., 3- (II), b.p. 160—167°/20 mm., and 2-methylcyclohexanone, b.p. 162°/18 mm., yield the corresponding NN-disubstituted hydrazines when hydrogenated; in the case of (II) the ketone and hydrazone are obtained, in addition.

R. T.

Autoxidation phenomena and valency tautomerism in the indone series. A. SCHÖNBERG and R. MICHAELIS (J.C.S., 1937, 109—112).—The properties, especially the presence of 1 active H (Zerevitinov), show that the supposed 2-anilo- (I), 2-*p*-dimethylaminoanilo- (II), and 2-*p*-methoxyanilo- (III) 3-phenyl- α -hydrindone of Pfeiffer *et al.* (A., 1935, 1369) are actually of the type 2-anilino-3-phenylindone (Ia, IIa, and IIIa). (IIa) (*methiodide*-, decomp. 226°) reacts in solution in its valency-tautomeric form $C_6H_4 \begin{smallmatrix} \text{CPh} \\ \diagup \text{CO} \end{smallmatrix} \text{C(NHR)} \cdots$, and its autoxidation (A., 1936, 1511) gives actually 1-hydroxy-3:4-diketo-1-phenyl-2-*p*-dimethylaminophenyl-1:2:3:4-tetrahydroisoquinoline (4-monoxime, sinters 180°, m.p. 192°). A similarly amended structure is applied to the oxidation product from (IIIa), and corresponding corrections in relation to the other reactions described by Pfeiffer *et al.* are suggested.

J. W. B.

Condensation of [aryl] propenyl ketones with ethyl oxalate. R. C. FUSON, R. E. CHRIST, and G. M. WHITMAN (J. Amer. Chem. Soc., 1936, 58, 2450—2452).—The Me group of Ph Δ^2 -propenyl ketone (I), b.p. 90—95°/2 mm. [from CHMe:CH:COCl

(II), C₆H₅, and AlCl₃ at 0° in light from a Hg-vapour lamp], possesses the expected reactivity, since (I), Et₂C₂O₄, and KOEt in Et₂O give the K salt (III) of *Et* α -diketo- ϵ -phenyl- Δ^2 -hexenoate, m.p. 106° (decomp.). (III) and BzCl in Et₂O afford *Et* ϵ -keto- α -benzoyloxy- ϵ -phenyl- Δ^2 -hexadienoate, m.p. 123°. Similarly, *mesityl* Δ^2 -propenyl ketone, b.p. 128°/5 mm. [from (II), *s*-C₆H₃Me₃, and AlCl₃ in CS₂], and Et₂C₂O₄ give *Et* α -diketo- ϵ -mesityl- Δ^2 -hexenoate, m.p. 156° (decomp.), oxidised (3% H₂O₂, 10% NaOH) to β -isodurylic acid. (I) gives a positive CHI₃-test; it is cleaved by hot aq. K₂CO₃ to COPhMe. H. B.

Action of alkalis on aryl and aryl alkyl ketones. N. KOZLOV, P. FEDOSEEV, and I. DRABKIN (J. Gen. Chem. Russ., 1936, 6, 1686—1689).—PhPr ^{β} in CS₂ and *p*-C₆H₄Me·COCl in presence of AlCl₃ (24 hr. at 100°) yield 4-methyl-4'-isopropylbenzophenone (I), b.p. 338—340°. *s*-C₆H₃Ph₃ and BzCl similarly give 2:4:6-triphenylbenzophenone (II), m.p. 168°. The products obtained by heating the ketones at 250—270° (1 hr.) with KOH are: from (I), *p*-C₆H₄Me·CO₂H (III) and *p*-C₆H₄Pr ^{β} ·CO₂H; from (II), *s*-C₆H₃Ph₃ and BzOH; from *p*-methylbenzophenone, (III) and BzOH; from COPhMe, CH₄ and BzOH; from *p*-methyl-, (III) and CH₄, and from *p*-ethyl-acetophenone, *p*-C₆H₄Et·CO₂H and CH₄.

R. T.

cyclopentane derivative from $\alpha\delta$ -dibromo- $\alpha\delta$ -dibenzoylbutane. R. C. FUSON, A. LIPPERT, R. V. YOUNG, and H. H. HULLY (J. Amer. Chem. Soc., 1936, 58, 2633—2634; cf. this vol., 24).—3-Cyano-6-benzoyl-2-phenyl-5:6-dihydro-1:4-pyran (I) (A., 1932, 63) (from $\alpha\delta$ -dibromo- $\alpha\delta$ -dibenzoylbutane and NaCN) is converted by 85% H₃PO₄ + a little 95% EtOH (first at room temp. and then at the b.p.) into 3-benzoyl-2-phenylcyclopentanone (II). The mechanism is probably: (I) \rightarrow 3-CO₂H derivative \rightarrow δ -hydroxy- $\alpha\delta$ -dibenzoylvaleric acid \rightarrow α -hydroxy- $\alpha\delta$ -dibenzoylbutane \rightarrow 1:2-dihydroxy-3-benzoyl-2-phenylcyclopentane \rightarrow (II). The similar conversion of β -benzoyloxy- $\alpha\zeta$ -diketo- $\alpha\zeta$ -diphenylhexane (III), m.p. 110—111°, into (II) supports this scheme. δ -Bromo- δ -benzoylvaleric acid, m.p. 109—110° (from the CO₂ acid and Br in CCl₄) (as chloride), with C₆H₄ and AlCl₃ at 0°—room temp. gives β -bromo- $\alpha\zeta$ -diketo- $\alpha\zeta$ -diphenylhexane, m.p. 62—63°, converted by NaOBz in aq. EtOH into (III).

H. B.

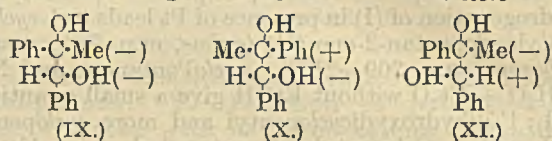
Demethylations and demethylenations. P. PFEIFFER and W. LOEWE (J. pr. Chem., 1937, [ii], 147, 293—310; cf. A., 1928, 420).—Simple aromatic OMe-compounds are readily demethylated by AlBr₃ in boiling C₆H₆; CO, CHO, and CO₂H do not influence the course of the reaction significantly except that in calculating the quantity of AlBr₃ it must be recognised that CO⁺ and CO₂H both react with AlBr₃. If CH₂ is interposed between CO and Ph the yield of demethylated product remains good but a chain of 2 CH₂ is disadvantageous; if a chain of 4 CH₂ is present a normal product of demethylation cannot be isolated. With unsaturated, aromatic OMe-ketones AlBr₃ is useful provided only one ethylenic linking is present; if two such are vicinal to CO the yield of OH-compound is minimal. In general demethylenation resembles demethylation but the yields are poorer. The demethylation of 2-, 3-, and 4-methoxy-, 4-ethoxy-,

2 : 4- and 4 : 4'-dimethoxy-benzophenone is described. *p*-Toluenesulphonamidobenzophenone is converted by Me_2SO_4 and 50% KOH in MeOH into *p*-toluenesulphon-methylamidobenzophenone, m.p. 119°, hydrolysed by conc. H_2SO_4 at 100° to *p*-methylaminobenzophenone, m.p. 111°, which is not demethylated by AlBr_3 in boiling C_6H_6 . *p*- $\text{C}_6\text{H}_4\text{Bz}\cdot\text{NMe}_2$ is similarly unaffected whereas *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}\cdot p'$ affords *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}\cdot p'$. *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ behave normally whereas *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is unchanged in boiling C_6H_6 but converted into *p*-hydrocoumaric acid, m.p. 127—129° from boiling PhMe. 3 : 4-(CH_2O_2) $\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ and 3 : 4-(CH_2O_2) $\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ are demethylated but very extensive decomp. occurs with 3 : 4-(CH_2O_2) $\text{C}_6\text{H}_3\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ and 3 : 4-(CH_2O_2) $\text{C}_6\text{H}_3\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$. 3 : 4-Methylenedioxy-benzpiperidine is converted into *protocatechupiperidine*, m.p. 187.5°. The reaction with methylenecaffeipiperidine, tetrahydropiperine, or piperine is either unsuccessful or complex. Caffeine and hydrohydrastinine are unaffected whereas papaverine gives a substance (sulphate, $\text{C}_{17}\text{H}_{15}\text{O}_4\text{N}_2\cdot\text{H}_2\text{SO}_4$). Piperonal affords *protocatechualdehyde*. 2 : 4-(NO_2) $\text{C}_{10}\text{H}_5\cdot\text{OMe}$ yields 2 : 4-(NO_2) $\text{C}_{10}\text{H}_5\cdot\text{OH}$ but $\beta\text{-C}_{10}\text{H}_7\cdot\text{OPh}$ is unaffected. H. W.

Optically active methyl- and ethyl-benzoin. A. MCKENZIE and A. RITCHIE (Ber., 1937, 70, [B], 23—36).—Under defined conditions, *r*-atrolactamide is converted by MgPhBr in Et_2O into *r*-methylbenzoin (I), m.p. 65—66°, identical with that derived from MgMeI and benzil. (+)-Atrolactic acid gives the corresponding *Me* ester, b.p. 107—108°/4 mm., $[\alpha]_{\text{D}}^{20} +32.1^\circ$, $[\alpha]_{\text{D}}^{18.3} +37.4^\circ$, $[\alpha]_{\text{D}}^{16.9} +74.8^\circ$, slowly transformed by aq. NH_3 at room temp. into (—)-atrolactamide (II), m.p. 62—63°, $[\alpha]_{\text{D}}^{17} -12.6^\circ$, $[\alpha]_{\text{D}}^{17.461} -14.5^\circ$ in COMe_2 . (+)-Atrolactamide (III) has m.p. 62.5—63.5°, $[\alpha]_{\text{D}}^{17} +12.6^\circ$, $[\alpha]_{\text{D}}^{17.461} +14.8^\circ$ in COMe_2 . (II) is transformed by MgPhBr into non-cryst. (—)-benzoylphenylmethylcarbinol (IV) (methylbenzoin), $[\alpha]_{\text{D}}^{20} -260.1^\circ$ in COMe_2 , -176.6° in EtOH, accompanied by much $\text{CPh}_2\text{Me}\cdot\text{OH}$ arising thus: $\text{OH}\cdot\text{CPhMe}\cdot\text{CO}\cdot\text{NH}_2 \rightarrow \text{MgBr}\cdot\text{O}\cdot\text{CPhMe}\cdot\text{CN} \rightarrow \text{MgBr}\cdot\text{O}\cdot\text{CPh}_2\text{Me} \rightarrow \text{CPh}_2\text{Me}\cdot\text{OH}$. Owing to the absence of mobile H, (IV) is not racemised by KOH-EtOH at room temp. Treatment of (IV) with MgPhBr affords (+)- α - β -triphenyl- β -methyl-ethylene glycol, m.p. 81—82°, $[\alpha]_{\text{D}}^{19} +76.6^\circ$, $[\alpha]_{\text{D}}^{18.61} +89^\circ$ in EtOH. (—)- α - β -Triphenyl- β -methyl-ethylene glycol, has m.p. 81—82°, $[\alpha]_{\text{D}}^{20.9} -75.9^\circ$, $[\alpha]_{\text{D}}^{20.6} -88.2^\circ$ in EtOH. *r*- α -Hydroxy- α -phenyl-n-butyric acid (V), m.p. 129—131°, obtained from BzCO_2H and MgEtBr in Et_2O , is transformed successively into the *Me* ester, b.p. 115—118°/6 mm., the *amide*, m.p. 91—91.5°, and *r*-benzoylphenylethylcarbinol (*r*-ethylbenzoin), m.p. 68—69°, also with some difficulty from benzil and MgEtBr . (V) is resolved by quinine in EtOH into (+)- α -hydroxy- α -phenyl-n-butyric acid, m.p. 128—129°, $[\alpha]_{\text{D}}^{20} +32.3^\circ$, $[\alpha]_{\text{D}}^{20.461} +38.1^\circ$ in H_2O , $[\alpha]_{\text{D}}^{20} +28.7^\circ$, $[\alpha]_{\text{D}}^{20.461} +35.7^\circ$ in COMe_2 , $[\alpha]_{\text{D}}^{20} +32.7^\circ$, $[\alpha]_{\text{D}}^{20.461} +39.9^\circ$ in EtOH, which gives the *Me* ester, b.p. 127°/17 mm., $[\alpha]_{\text{D}}^{20} +24.7^\circ$, $[\alpha]_{\text{D}}^{20.791} +26.2^\circ$, $[\alpha]_{\text{D}}^{20} +31.1^\circ$, $[\alpha]_{\text{D}}^{20.338} +65.6^\circ$, the (—)-*amide*, m.p. 91.5—92°, $[\alpha]_{\text{D}}^{20} -15^\circ$, $[\alpha]_{\text{D}}^{20.461} -19^\circ$ in COMe_2 , and thence $\text{CPh}_2\text{Et}\cdot\text{OH}$, m.p. 94—95°, and (—)-benzoylphenyl-

ethylcarbinol [(—)-ethylbenzoin], m.p. 69—70°, $[\alpha]_{\text{D}}^{17} -191.3^\circ$, $[\alpha]_{\text{D}}^{17.591} -201.5^\circ$, $[\alpha]_{\text{D}}^{17.5461} -241.4^\circ$ in COMe_2 , $[\alpha]_{\text{D}}^{17} -199.3^\circ$, $[\alpha]_{\text{D}}^{17.591} -210.9^\circ$, $[\alpha]_{\text{D}}^{17.5461} -250.8^\circ$ in EtOH, $[\alpha]_{\text{D}}^{15} +145.8^\circ$, $[\alpha]_{\text{D}}^{17.591} +154.3^\circ$, $[\alpha]_{\text{D}}^{17.5461} +180.5^\circ$ in CS_2 , which is not racemised by KOH-EtOH. The inadequacy of the present nomenclature for substances of this type is pointed out.

In attempts to establish the configurative relationship between $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ and $\text{OH}\cdot\text{CPhMe}\cdot\text{CO}_2\text{H}$, (I) is found to be reduced by Al-Hg , Zn dust and NaOH, or Na-Hg to a mixture of *r*- α - (VI) and *r*- β - (VII)-methylhydrobenzoin and by H_2 (Pt) to cryst. (VI) doubtless containing a small proportion of (VII). (IV) gives a laevorotatory mixture (VIII) of the two corresponding diastereoisomeric glycols when reduced by H_2 . For these the configurations (IX) and (X) are possible and (IX) is tentatively assigned to the β -glycol. (VIII) is regarded as a mixture of (IX) and (XI) [mirror image of (X)] since it has $[\alpha]_{\text{D}}^{20.993} -33^\circ$.



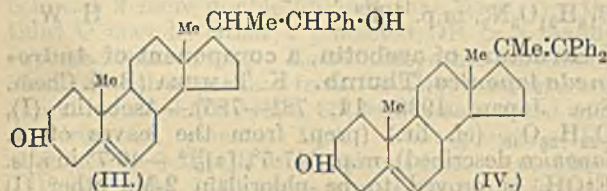
Since the prep. of (IV) from the acid does not involve change of configuration and since (—)- $\text{OH}\cdot\text{CHPhBz}$ and (—)- $\text{CHPhAc}\cdot\text{OH}$ are derived from (—)- $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ without configurative change and a laevorotatory mixture of glycols is obtained from (IV) whereas the glycols from (—)- $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ and (—)- $\text{CHPhAc}\cdot\text{OH}$ are the optically homogeneous, dextrorotatory α - or β -glycols, it appears that (+)- $\text{OH}\cdot\text{CPhMe}\cdot\text{CO}_2\text{H}$ and (—)- $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ have opposite configurations in harmony with Freudenberg's views.

(I) is transformed by MgEtBr into *r*- α - β -diphenyl- β -methyl- α -ethylethylene glycol, b.p. 170—171°/5 mm. *r*-Atrolactamide and MgEtBr give COPhMe , $\text{OH}\cdot\text{CPhMe}\cdot\text{COEt}$ (2 : 4-dinitrophenylhydrazine, m.p. 140—141°), and $\text{CPhMeEt}\cdot\text{OH}$. H. W.

Attempted syntheses of natural sterols. II. Synthesis of 7-hydroxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene. G. HABERLAND and E. BLANKE (Ber., 1937, 70, [B], 169—171).—Interaction of $\text{CNaMe}(\text{CO}_2\text{Et})_2$ and β -6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthylethyl bromide in xylene at 150° followed by hydrolysis of the product with KOH gives methyl- β -6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthyl-ethylmalonic acid (I), m.p. 132—133°, which passes at 160° into γ -6-methoxy-1 : 2 : 3 : 4-tetrahydro-1-naphthyl- α -methylbutyric acid, b.p. 160° (bath)/0.03 mm., m.p. 96° (*amide*, m.p. 106°). (I) is dehydrogenated by S to γ -6-methoxy-1-naphthyl- α -methyl-n-butyric acid, m.p. 89° (*amide*, m.p. 144°), converted by 90% H_2SO_4 at room temp. into 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene, m.p. 108°, which is demethylated (48% HBr in AcOH) to 7-hydroxy-1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene. H. W.

17-iso- Δ^5 -Pregnen-3-ol-20-one. A. BUTENANDT and G. FLEISCHER (Ber., 1937, 70, [B], 96—102).—3-Acetoxybismorcholenic acid, $[\alpha]_{\text{D}}^{20} -73.5^\circ$ in CHCl_3 , exists in a stable form, m.p. 235—236°, and a labile modification, m.p. 224—226°, which rapidly passes

into the stable variety. The Me ester (I), $[\alpha]_D^{20} -61.9^\circ$ in CHCl_3 , forms leaflets, m.p. 138—139°, and stable prisms, m.p. 156—157°. Treatment of (I) with MgPhBr gives the corresponding diphenylcarbinol (II) and phenyl-3-hydroxy- Δ^5 -20-pregnenylcarbinol (III), m.p. 243°. (II) is converted by successive treatments with KOH-MeOH , AcOH , and Ac_2O into the acetate, m.p. 217°, of the alcohol (IV), m.p. 112°, transformed by Br in CHCl_3 and subsequent ozonisation into pregnenolone (V). (III) (diacetate, m.p. 220—221°) is con-



verted by the successive action of Br and CrO_3 in AcOH into Ph 3-keto-20- Δ^4 -pregnenyl ketone, m.p. 227—228°, $[\alpha]_D^{20} +86.58^\circ$ in dioxan (oxime, m.p. 208—209°). (V) is isomerised to the extent of about 30% by 5% KOH-MeOH to 17-iso- Δ^5 -pregnen-3-ol-20-one (VI), m.p. 172—173°, $[\alpha]_D^{20} -140.5^\circ$ in EtOH , which cannot be separated from unchanged (V) by crystallisation. More success is obtained by employment of the acetates but isopregnenolonyl acetate, m.p. 170—171°, $[\alpha]_D^{20} -126^\circ$ in EtOH , cannot be hydrolysed without isomerisation. In contrast with (V), (VI) yields a sparingly sol., additive compound with digitonin through which its isolation is achieved. H. W.

Corticosterone, a crystallised compound with the biological activity of the adrenal-cortical hormone. P. DE FREMERY, E. LAQUEUR, T. REICHSTEIN, R. W. SPANHOFF, and I. E. UYLDERT (Nature, 1937, 139, 26).—Further purification of the active substance obtained (A., 1936, 473, 1383) from the cortex of the adrenal gland yields a cryst. substance, m.p. 180—182° (corr.), $[\alpha]_D^{25} +223^\circ$ in EtOH , corticosterone, a highly active cortical hormone, the biological activity of which is described. L. S. T.

Synthesis of phenanthrene and hydrophenanthrene derivatives. VII. 1':3'-Diketo-5:9-dimethoxy-1:2-cyclopentenophenanthrene. L. F. FIESER and E. B. HERSHBURG (J. Amer. Chem. Soc., 1936, 58, 2382—2385).—A continuation of previous work (see this vol., 24). 1:5- $\text{C}_{10}\text{H}_8(\text{OMe})_2$, $(\text{CH}_2\text{CO})_2\text{O}$, and AlCl_3 in cold $\text{C}_2\text{H}_2\text{Cl}_4\text{-PhNO}_2$ give β -4:8-dimethoxy-1-naphthoylpropionic acid, m.p. 175—176° (Et ester, m.p. 53—53.5°), reduced (Clemmensen) to 20—25% of γ -4:8-dimethoxy-1-naphthylbutyric acid, m.p. 154—154.5° [Me, m.p. 65—65.5°, and Et (I), b.p. 201—203°/1 mm., m.p. 47—47.5°, esters], and some γ -8-methoxy-1:2:3:4-tetrahydro-1-naphthylbutyric acid (II), m.p. 74.5—75.5° [oxidised (alkaline KMnO_4) to 3-methoxyphthalic acid]. The oxalyl derivative from (I) is cyclised (78% H_2SO_4) to 5:9-dimethoxy-3:4-dihydrophenanthrene-1:2-dicarboxylic anhydride, m.p. 231—232° [corresponding Me_2 ester (III), m.p. 151—153°], dehydrogenated (S at 250—300°) to 5:9-dimethoxyphenanthrene-1:2-dicarboxylic anhydride (IV), m.p. 289—290° [corresponding Me_2 ester (V), m.p. 133—134°, prepared by dehydrogenation (S) of (III)]. (V) with $\text{EtOAc}+\text{Na}$ followed by

hydrolysis (dil. HCl) of the resultant Na derivative gives 1':3'-diketo-5:9-dimethoxy-1:2-cyclopentenophenanthrene, m.p. 281—283° (decomp.) (softens about 265°). (IV) heated with EtOH-HCl for 24 hr. yields Et₂ 5(or 9)-methoxy-9(or 5)-ethoxyphenanthrene-1:2-dicarboxylate, m.p. 109.5—110°, converted [as for (V)] into 1':3'-diketo-5(or 9)-methoxy-9(or 5)-ethoxy-1:2-cyclopentenophenanthrene, m.p. 207—208°. β -2:6-Dimethoxy-1-naphthoylpropionic acid, m.p. 156—156.5°, is reduced (modified Clemmensen) to γ -2:6-dimethoxy-1-naphthylbutyric acid, m.p. 122—124°; a by-product of type (II) could not be found. The products from the above reductions are remethylated prior to separation. 4-Methoxy-1-methylnaphthalene (picrate, m.p. 148—149°) has b.p. 164.5—165°/21 mm. Dehydrogenation (Se) of impure (II) gives α - $\text{C}_{10}\text{H}_7\text{-OMe}$ as the only identifiable product. All m.p. are corr. H. B.

Degradation of cholic acid to 3:7:12-trihydroxypregnan-20-one. H. MORSMAN, M. STEIGER, and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 3—16; cf. Shimizu and Kazuno, this vol., 20).—Gradual addition of Me cholate (improved prep.) in C_6H_6 to MgMeBr in Et_2O gives 3:7:12-trihydroxynorcholyldimethylcarbinol, m.p. 184—185° (corr.) [also $+1\text{H}_2\text{O}$, m.p. 126—130° (decomp.)], converted by protracted heating with Ac_2O in $\text{C}_6\text{H}_5\text{N}$ at 100° into the corresponding tetra-acetate, m.p. 108—111° (corr.), and by less drastic treatment at 55—60° into the triacetate, m.p. (indef.) 60—80° (cf. loc. cit.). Either acetate is oxidised by CrO_3 ($=6\text{O}$) in AcOH at 90—95° to triacetylnorcholic acid (I), m.p. 105—108°, $[\alpha]_D^{18} +86.5^\circ$ in abs. EtOH (Me ester, m.p. 70—71°), hydrolysed by $\text{KOH-H}_2\text{O-MeOH}$ to norcholic acid, m.p. 188—192° (corr.) from COMe_2 or m.p. 200° (corr.) from C_6H_6 . Me norcholate, m.p. (indef.) 110—125° and, after, re-solidification, m.p. 160—161°, $[\alpha]_D^{18} +37.5^\circ$ in abs. EtOH (also $+4\text{MeOH}$), is transformed by MgMeBr into 3:7:12-trihydroxybischolyldimethylcarbinol, m.p. 238—242° (corr.; decomp.), the tetra-acetate, m.p. 131—132°, of which is oxidised to non-cryst. triacetylbisnorcholic acid (II), whence bisnorcholic acid, m.p. 298—301° (corr.; decomp.), $[\alpha]_D^{18} +13.8^\circ$ in abs. EtOH . Diphenyl-3:7:12-trihydroxynorcholyldimethylcarbinol, m.p. 202—205° (corr.), $[\alpha]_D^{17} +23.8^\circ$ in abs. EtOH , is transformed into the non-cryst. acetate, which is oxidised to (I); it is converted by I in boiling C_6H_6 or by boiling mineral acid into diphenyl-3:7:12-trihydroxynorcholyldimethane, m.p. 220—230°, $[\alpha]_D^{18} +52.8^\circ$ in abs. EtOH , the triacetate, m.p. 83—85°, of which is ozonised or oxidised mainly to (I). Diphenyl-3:7:12-trihydroxybischolyldimethylcarbinol gives a non-cryst. acetate, oxidised to (II). Me bisnorcholate ($+0.5\text{H}_2\text{O}$), m.p. 97—98° and m.p. 156—159° after re-solidification at about 125—140°, $[\alpha]_D^{17} +22.0^\circ$ in abs. EtOH , is transformed by MgPhBr into the corresponding non-cryst. carbinol and thence by Ac_2O in $\text{C}_6\text{H}_5\text{N}$ into diphenyl-3:7:12-triacetoxybischolyldimethylcarbinol, m.p. 252° (corr.), $[\alpha]_D^{18} +23.11^\circ$ in abs. EtOH , which is dehydrated by AcOH at 165° to α -diphenyl- β -methyl- β -3:7:12-triacetoxyethiocholyldimethylcarbinol, m.p. 182—183° (corr.), $[\alpha]_D^{20} +423.6^\circ$ in abs. EtOH . This is converted by ozonisation in CHCl_3 followed by treatment with Zn

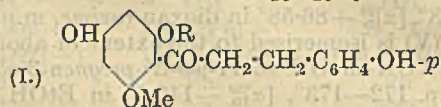
filings and AcOH into the hygroscopic 3:17:12-triacetoxypregnan-20-one, m.p. 134—135° (corr.), $[\alpha]_D^{25} +120.7^\circ$ in abs. EtOH, whence 3:7:12-trihydroxypregnan-20-one, m.p. 120—127° (decomp.), $[\alpha]_D^{25} +107.75^\circ$ in abs. EtOH. H. W.

General method of preparing α -amino- and α,γ -diamino-keto-compounds. II. P. W. NEBER, A. BURGARD, and W. THIER (Annalen, 1936, 526, 277—294; cf. A., 1935, 345).—The method could not be successfully applied to 3:4-dihydroxyacetophenone-oxime, m.p. 184° (decomp.), 3:4-diacetoxyacetophenone, m.p. 91°, 3:4-dibenzoyloxyacetophenone, m.p. 118°, or 3:4-dimethoxyacetophenone-oxime, m.p. 144°; the last is converted by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ into 3:4-dimethoxyacetanilide, m.p. 133°. 3:4-Methylenedioxyacetophenone-oxime is transformed by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in well-cooled $\text{C}_5\text{H}_5\text{N}$ into the unstable $p\text{-toluenesulphonate}$, m.p. 75° (decomp.), which is transformed by KOEt-EtOH into ω -amino-3:4-methylenedioxyacetophenone [hydrochloride (I), m.p. 193°]. Piperonal and MeNO_2 in presence of KOH-EtOH afford α -nitro- β -3:4-piperonylethylene, m.p. 161° (with the corresponding nitro-alcohol, $\text{C}_9\text{H}_9\text{O}_5\text{N}$, m.p. 94°), transformed by Br in boiling CHCl_3 into β -bromo- α -nitro- β -3:4-piperonylethylene, m.p. 98—99°, which is converted by KOH in boiling MeOH into ω -nitroacetopiperone, m.p. 172°, hydrogenated (PtO_2 in AcOH) to (I). $\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ is unsuited to the isomerisation on account of its ready passage into methylisooxazolone but acetoacetanilide-oxime is transformed into its $p\text{-toluenesulphonate}$, m.p. 128° (decomp.), converted by KOEt-EtOH followed by 2N-HCl into α -aminoacetoacetanilide hydrochloride (corresponding sulphate) which on treatment with alkali gives the diazine, $\text{NHPh}\cdot\text{CO}\cdot\text{CH}\langle\text{CMe}\cdot\text{N}\rangle\text{CH}\cdot\text{CO}\cdot\text{NHPh}$, m.p. 222° (decomp.). $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ at 160° give acetoacet- p -dimethylaminoanilide, m.p. 113°, the oxime, m.p. 137° (decomp.), of which could not be converted into the $p\text{-toluenesulphonate}$. Acetoacet- p -nitroanilide, m.p. 124°, is converted by NaNO_2 and H_2SO_4 into oximinoacetoacet- p -nitroanilide, m.p. 185° (decomp.). 1-Hydrindone-oxime gives the $p\text{-toluenesulphonate}$, m.p. 157° (decomp.), and thence 2-amino-1-hydrindone (hydrochloride, decomp. $>240^\circ$; picrate, decomp. 156°) in good yield. 1-Oximino-1:2:3:4-tetrahydronaphthalene $p\text{-toluenesulphonate}$, m.p. 96°, yields 2-amino-1-keto-1:2:3:4-tetrahydronaphthalene hydrochloride, decomp. 117°, in 72% yield. 6-Phenyl-2:2-dimethyl-4-piperidone is transformed by Me_2SO_4 and anhyd. Na_2CO_3 into 6-phenyl-1:2:2-trimethyl-4-piperidone, m.p. 78°, and thence successively into its oxime, two (?) stereoisomeric forms, m.p. 181—182° and 164—165° respectively, its $p\text{-toluenesulphonate}$, m.p. 107° (decomp.), and the non-cryst. 5-amino-6-phenyl-1:2:2-trimethyl-4-piperidone (very hygroscopic hydrochloride). 2:6-Diphenyl-1-methylpiperidone-4-oxime, m.p. 190°, yields a $p\text{-toluenesulphonate}$, m.p. 98°, and 2-naphthalene-sulphonate, m.p. 120° (decomp.), which give 5-amino-2:6-diphenyl-1-methylpiperidone dihydrochloride, decomp. 130° after softening at 90°, converted by dil. alkali into the "dihydrodiazine," $\text{C}_{36}\text{H}_{36}\text{N}_4$, m.p.

187° (decomp.) after becoming yellow at 160°. ϵ Methylamino- α -diphenyl- Δ^5 -penten- γ -one, m.p. 100°, is incidentally described.

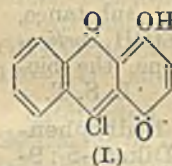
Acetoneoxime $p\text{-toluenesulphonate}$ is converted by successive treatment with KOEt-EtOH and BzCl into benzamidoacetone, m.p. 85°, the oxime (II), m.p. 136°, of which is transformed through its unstable $p\text{-toluenesulphonate}$, m.p. 74° (decomp.), into α -amino- γ -benzamidoacetone hydrochloride, m.p. 207°. (II) is converted by $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_2\text{Cl}$ into a substance, $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}_3$, m.p. 183°. H. W.

Structure of asebotin, a component of *Andromeda japonica*, Thunb. K. TAMURA (Bull. Chem. Soc. Japan, 1936, 11, 781—785).—Asebotin (I), $\text{C}_{22}\text{H}_{26}\text{O}_{10}$ (cf. lit.) (prep. from the leaves of *A. japonica* described), m.p. 147.5°, $[\alpha]_D^{25} -46.7^\circ$ in abs. EtOH, is proved to be phloridzin 2-Me ether (I) ($\text{R} = \text{glucose residue}$). (I) and 5% H_2SO_4 at 100° give glucose and asebogenin, $\text{C}_{16}\text{H}_{16}\text{O}_5$ (cf. lit.), m.p.



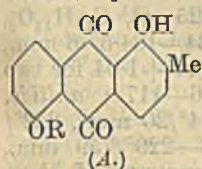
168° (Ac_2O derivative, m.p. 76—77°); the aglucone and KOH at 170—180° give phloretic acid and phloroglucinol Me ether (II). (II) and phloretonitrile give (Hoesch) isoasebogenin (2:4:4'-trihydroxy-6-methoxy- β -phenylpropionophenone), m.p. 201—202°. (I) and $\text{MeI}\cdot\text{K}_2\text{CO}_3\cdot\text{COMe}_2$ give a viscous ether, hydrolysed by acid to 2-hydroxy-4:6:4'-trimethoxy- β -phenylpropionophenone, m.p. 109—110°. R. S. C.

Synthesis of anaquinones. H. WALDMANN and H. POPPE (Annalen, 1937, 527, 190—194).—Gradual addition of a mixture of 1:4- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{OH}$ and maleic anhydride to molten $\text{AlCl}_3\cdot\text{NaCl}$ at 180—220° gives 10-chloro-1-hydroxy-4:9-anthraquinone (I), m.p. 205—206°, identical with that obtained from SOCl_2 and quinzarin. Similarly citraconic anhydride (II) and 1:4- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{OH}$ give the isomeric 10-chloro-1-hydroxy-2(or 3)-methyl-4:9-anthraquinones-A, m.p. 202° (acetate, m.p. 210.5°), and -B (III), m.p. 174—175° [acetate (IV), m.p. 212°]. $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ and toluquinol yield 1:4-dihydroxy-2-methylanthraquinone (V), m.p. 175° (acetate, m.p. 213°, identical with (IV)), converted by SOCl_2 into (III). (V) is obtained from naphthaquinol and (II). H. W.



Aspergillus colouring matters. I. H. RAISTRICK, R. ROBINSON, and A. R. TODD (J.C.S., 1937, 80—88).—Flavoglucin, $\text{C}_{19}\text{H}_{28}\text{O}_3$ (I) [2:4-dinitrophenylhydrazone, m.p. 179—181°, and a form, m.p. 186—187°; substance, $\text{C}_{25}\text{H}_{31}\text{O}_3\text{N}_2$, m.p. 137°, by the action of an excess of NHPhNH_2 ; substance, $\text{C}_{25}\text{H}_{34}\text{O}_3\text{N}_2$, m.p. 161°, by interaction with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, contains 2 OH (Zerevitinov) and gives $\text{H}_2\text{C}_2\text{O}_4$, n -octoic acid (showing presence of a $\text{CH}_3\cdot[\text{CH}_2]_6\cdot\text{C}:$ group), AcOH (?), and unidentified acids when oxidised with 4% $\text{KMnO}_4\text{-C}_5\text{H}_5\text{N}$ at room temp. Auroglucin, $\text{C}_{19}\text{H}_{22}\text{O}_3$ (II), m.p. 153°, gives a 2:4-dinitrophenylhydrazone, m.p. 223—224°, phenylurethane, m.p. 161°, substance, m.p. 108—109°,

obtained with Ac_2O , and a substance, $\text{C}_{25}\text{H}_{28}\text{O}_2\text{N}_2 + \text{H}_2\text{O}$, m.p. 185° (decomp.), by the action of $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$. Partial hydrogenation of (I) (3H_2) and of (II) (6H_2) affords the same product, m.p. 111° , consisting mainly of an unsaturated alcohol, $\text{C}_{19}\text{H}_{32}\text{O}_2$ (phenylurethane, sinters 157° , m.p. $160-161^\circ$). Complete hydrogenation (Pt-SiO₂) of (I) and (II) requires 7H_2 and 10H_2 , respectively: the product, b.p. $173-175^\circ/12\text{ mm.}$, so obtained from (I) appears to be a mixture of an alcohol $\text{C}_{19}\text{H}_{38}\text{O}$ and $\text{C}_{19}\text{H}_{38}$. (II) thus contains 3 more double linkings than does (I): the third O may be either a protected OH or a readily ruptured ether linking. Emodin Me, ether (physcion), identical with a specimen from *Ventilago madraspatana* (Perkin et al., J.C.S., 1894, 65, 943), was isolated with (I) from *A. glaucus*, Link. Rubroglauin (III), $\text{C}_{18}\text{H}_{12}\text{O}_5 + 0.5\text{EtOH}$ and solvent-free, m.p. $180-181^\circ$ (A., 1934, 1263, gives m.p. $172-173^\circ$), isolated from *A. ruber*, *A. albidus*, and *A. glaucus alba*, gives a Ac_2 derivative, $+ \text{H}_2\text{O}$, m.p. $226-228^\circ$, and affords 2-methylantracene when distilled with Zn dust; (I) is therefore a dihydroxymethoxymethylantraquinone. Demethylation of (III) with conc. H_2SO_4 at $140-150^\circ$ gives a substance, $\text{C}_{15}\text{H}_{10}\text{O}_5 + \text{H}_2\text{O}$, m.p. 220° (Ac_3 derivative), probably (A) ($\text{R} = \text{H}$, Me at



2, 3, or 7), since it is different from 1:3:4-trihydroxy-2-methylantraquinone $+ \text{H}_2\text{O}$ (IV), m.p. approx. $268-270^\circ$ (partial sublimation), synthesised as follows: resacetophenone with KOH-MeOH-MeI gives 2-hydroxy-4-methoxy-3-methylacetophenone, converted by $\text{N-NaOH-MeOH-3\% H}_2\text{O}_2$ (under H_2) and subsequent methylation into 2:3:6-trimethoxytoluene, b.p. $145-147^\circ/14\text{ mm.}$, converted by $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O-AlCl}_3$ in CS_2 into $\text{o-(2':5'-dimethoxy-p'-toluoyl)benzoic acid}$, m.p. $205-208^\circ$, cyclised by conc. H_2SO_4 at $150-160^\circ$ to (IV). (III) is probably A ($\text{R} = \text{Me}$). J. W. B.

Aminoanthraquinone dyes derived from tetrachloroquinizarin. H. WALDMANN (J. pr. Chem., 1937, [ii], 147, 326-330).—5:6:7:8-Tetrachloro-1:4-dimethoxyanthraquinone is converted by $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ and KOAc in PhNO_2 containing $\text{Cu}(\text{OAc})_2$ at $200-210^\circ$ into 6:7-dichloro-5:8-di-p-toluenesulphonamido-1:4-dimethoxyanthraquinone, m.p. 255° (decomp.), transformed by conc. H_2SO_4 at room temp. into 6:7-dichloro-5:8-diamino-1:4-dimethoxyanthraquinone, decomp. about 290° , which is demethylated by conc. H_2SO_4 at 120° to 6:7-dichloro-5:8-diaminoquinizarin, decomp. 285° . 5:8-Di-p-toluenesulphonmethyamido-1:4-dimethoxyanthraquinone and conc. H_2SO_4 yield 5:8-di(methylamino)-1:4-dimethoxyanthraquinone, m.p. 300° (decomp.), which with H_3BO_3 in conc. H_2SO_4 at 120° gives 5:8-di(methylamino)quinizarin, m.p. $>310^\circ$. 6:7-Dichloro-5:8-di-p-toluenesulphonamido-1:4-dimethoxyanthraquinone and $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ in $\text{o-C}_6\text{H}_4\text{Cl}_2$ containing K_2CO_3 at $170-180^\circ$ afford 6:7-dichloro-5:8-di-p-toluenesulphonmethyamido-1:4-dimethoxyanthraquinone, decomp. 245° , whence 6:7-dichloro-5:8-di(methylamino)-1:4-dimethoxyanthraquinone, decomp. 186° , and 6:7-dichloro-5:8-di(methylamino)quinizarin, decomp. 249° . H. W.

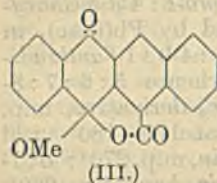
5:6:7:8-Tetrachloroquinizarin and 5:6:7:8-tetrachloro-1:2-benzanthraquinone. H. WALDMANN (J. pr. Chem., 1937, [ii], 147, 331-337).—Gradual addition of a mixture of $\text{C}_6\text{Cl}_4(\text{CO})_2\text{O}$ and quinol to $\text{AlCl}_3\text{-NaCl}$ at $130-135^\circ$, subsequently raised to $150-155^\circ$, gives 3':4':5':6'-tetrachloro-2:5-dihydroxybenzophenone-2-carboxylic acid, m.p. 231° (yield 82%); if the temp. of the mixture is raised to $210-215^\circ$, 5:6:7:8-tetrachloroquinizarin (I), m.p. 247° , is obtained almost quantitatively. (I) is transformed by $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ and Na_2CO_3 in $\text{o-C}_6\text{H}_4\text{Cl}_2$ at 170° into 5:6:7:8-tetrachloro-1:4-dimethoxyanthraquinone (II), m.p. 290° , and by $\text{Pb}(\text{OAc})_4$ in AcOH into 5:6:7:8-tetrachloro-1:4:9:10-anthradiquinone, m.p. 250° (decomp.), whence 5:6:7:8-tetrachloropurpurin, m.p. 265° (Ac_3 derivative, m.p. 208°). (I), NH_2Ph , and NaOAc at $170-180^\circ$ yield 6:7-dichloro-5:8-dianilinoquinizarin, m.p. 270° ; 6:7-dichloro-5:8-di-p-toluidinoquinizarin has m.p. 260° . 6:7-Dichloro-5:8-dianilino-1:4-dimethoxyanthraquinone, m.p. 265° , is obtained from (II). (I) is reduced by $\text{Sn} + \text{HCl}$ in boiling AcOH to tetrachlorohydroquinizarin, $\text{C}_{14}\text{H}_6\text{O}_4\text{Cl}_4$, m.p. 254° , transformed by NH_2Ph and H_3BO_3 at 100° into 5:6:7:8-tetrachloro-1:4-dianilinoanthraquinone, m.p. 295° after softening.

Tetrachloro- α -naphthoylbenzoic acid in PhNO_2 is transformed by P_4O_{10} at $150-160^\circ$ into 5:6:7:8-tetrachloro-1:2-benzanthraquinone, m.p. 254° , converted by $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ into 6:7-dichloro-5:8-di-p-toluenesulphonamido-1:2-benzanthraquinone, decomp. $245-246^\circ$, whence 6:7-dichloro-5:8-diamino-1:2-benzanthraquinone, m.p. 276° , converted by anhyd. NaOAc , Cu powder, and C_{10}H_8 at 220° into dichlorodiaminodibenzindanthrone, $\text{C}_{36}\text{H}_{18}\text{O}_4\text{N}_4\text{Cl}_2$. H. W.

Condensations of the anhydride of 1:4-dihydroxyanthraquinone-2:3-dicarboxylic acid. C. MARSCHALK (Bull. Soc. chim., 1937, [v], 4, 184-193).—The anhydride (I) of 1:4-dihydroxyanthraquinone-2:3-dicarboxylic acid (II) reacts with NH_2Ph in AcOH at room temp. to give the NH_2Ph salt of 2-carbanilyl-1:4-dihydroxyanthraquinone-3-carboxylic acid (III) which is liberated by HCl . Boiling AcOH converts (III) into a mixture of the (less sol.) phenylimide (IV) of (II) [best obtained by adding NH_2Ph to (I) in PhNO_2 at 200°] and 2-carbanilyl-1:4-dihydroxyanthraquinone, also obtained by heating (I) with an excess of NH_2Ph in PhNO_2 , by decarboxylation of (III) with $\text{Na}_2\text{S}_2\text{O}_4\text{-NaHCO}_3$, or by the action of NH_2Ph on 1:4-dihydroxyanthraquinone-2-carboxyl chloride. Similar condensation is effected between (I) and o- , m- , and $\text{p-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ in AcOH to give derivatives of type (IV). Condensation of (I) with C_6H_6 or its appropriate derivative in presence of AlCl_3 affords 2-benzoyl-, m.p. $263-264^\circ$ (V), 2-p-toluy-, m.p. $245-246^\circ$, and 2-p-chlorobenzoyl-, m.p. $260-261^\circ$, -1:4-dihydroxyanthraquinone-3-carboxylic acid, decarboxylated (boiling $\text{C}_2\text{H}_5\text{N}$ or $\text{Na}_2\text{S}_2\text{O}_4\text{-NaHCO}_3$) to give, respectively, 2-benzoyl-, m.p. $185-186^\circ$, 2-p-toluy-, m.p. $189-190^\circ$, and 2-p-chlorobenzoyl-, m.p. $257-258^\circ$, -1:4-dihydroxyanthraquinone. (V) is hydrolysed by boiling 5% NaOH to quinizarin. J. W. B.

ψ -Form of methyl 2:3-benzanthraquinone-1-carboxylate. H. WALDMANN and R. KRETSCH

(Ber., 1937, 70, [B], 102—105).—1-Amino-2:3-benzanthraquinone is converted into 1-cyano-2:3-benzanthraquinone, m.p. 295.5°, hydrolysed by H_2SO_4 at 175° to 2:3-benzanthraquinone-1-carboxylic acid (I), m.p. 282°, converted by PCl_5 or SOCl_2 into the chloride (II), decomp. about 245°. Esterification of (I) is not readily effected by HCl-MeOH and *Me* 2:3-benzanthraquinone-1-carboxylate, m.p. 223°, is best obtained by heating *K* 2:3-benzanthraquinone-1-carboxylate with KMeSO_4 at 200° or from freshly prepared (II) and boiling MeOH . At room temp. (II) and MeOH give *Me* μ -2:3-benzanthraquinone-1-carboxylate (II), m.p. 193°, which is unchanged by short boiling with MeOH , partly isomerised by $\text{H}_2\text{SO}_4\text{-MeOH}$, and completely isomerised by boiling HCl-MeOH . (II) with C_6H_6 and sublimed FeCl_3 affords 9-hydroxy-9-phenyl-2:3-benzoanthrone-1-carboxylactone, m.p. 199°.



Gland secretion of alligators (yacarol).—See A., III, 88.

Catalytic hydrogenation of α -ionone; ionol, dihydroionol, tetrahydroionol, dihydroionone, tetrahydroionone. L. PALFRAY, S. SABETAY, and J. KANDEL (Compt. rend., 1936, 203, 1376—1378).— α -Ionone (I) with Ni-H_2 under pressure at 65° affords dihydro- α -ionone (A., 1934, 659) [semicarbazone, m.p. 171—172° (block)]; at 90° dihydro- α -ionol is also formed. At 150—240°, tetrahydroionol (A., 1919, i, 540) (allophanate, m.p. 164°) is formed, which when oxidised (CrO_3) affords tetrahydroionone. α -Ionol (II), b.p. 103°/3 mm. (nitrobenzoyl derivative, m.p. 62.5°), is prepared from α -ionone and $\text{Al(OPr}^i)_3$ and is oxidised (CrO_3) to (I). (I) and (II), but not the other reduction products, give the same colour reaction with $\text{CCl}_3\text{-CHO}$ and HCl .

Menthylamines. G. VAVON and I. CHILOUET (Compt. rend., 1936, 203, 1526—1528).—Since the NH_2 is closer in space to Pr^i in neomenthylamine (I), the latter reacts more slowly than menthylamine with benzyl and trimethylbenzyl bromide, benzyl oxalate, and piperonal, and its formyl derivative is hydrolysed (alkali) more slowly (cf. A., 1926, 1147; 1927, 1080; 1931, 229; 1935, 88). This accounts for the difficulty in reducing neomenthoneoxime and for the reaction of (I) with HNO_2 (cf. A., 1931, 954).

M.p. graphs of bornyl fumarates. E. B. ABBOT, A. MCKENZIE, and J. D. MCB. ROSS (Ber., 1937, 70, [B], 163—168).—The m.p. graph of mixtures of (—)-bornyl fumarate (I) and *r*-bornyl fumarate exhibits two min. and a max. showing that the externally compensated ester is correctly described as racemic. The m.p. graph of mixtures of (+)-bornyl H fumarate and the optically inactive ester shows the racemic compound to be dissociated to the extent of 17%. The rectilinear course from 0% to 25% of (+)-ester indicates the formation of mixed crystals of (+)- and (—)-ester whereas between 25% and 50% of (+)-ester the production of a racemic compound is indicated. The graph of the m.p. of

mixtures of (I) and (—)-bornyl (+)-bornyl fumarate (II) indicates the production of a partial racemate, m.p. 107.9°, which is unstable in the presence of an excess of (II) and is dissociated to a considerable extent.

H. W.

Bornylamines. G. VAVON and I. CHILOUET (Compt. rend., 1937, 204, 53—55; see above).—Camphorimine with Pt-H_2 affords neobornylamine (I), isolated as the hydrochloride, in good yield, but the oxime reacts with difficulty. (I) reacts with CH_2PhBr , trimethylbenzyl bromide, benzyl oxalate, and piperonal less readily than does bornylamine. The formyl derivative of (I) is the less easily hydrolysed and is assigned the *cis*-structure (cf. A., 1926, 1042).

J. L. D.

Constitution of shonanic acid, one of the two characteristic volatile acids from the wood of *Libocedrus formosana*, Florin. I. Isolation of shonanic acid and its general properties. N. ICHIKAWA (Bull. Chem. Soc. Japan, 1936, 11, 759—769).—Extraction of the wood of *L. formosana* with 5% aq. NaOH , steam-distillation of the acidified solution, etc. gives 0.015% of phenols and 0.42% of acids, which (508 g.) yield by fractional distillation and crystallisation shonanic acid (I) (325 g.), $\text{C}_{10}\text{H}_{14}\text{O}_2$, m.p. 40—41°, b.p. 264°/754 mm., 134—134.5°/6 mm., $[\alpha]_D^{25} -0.75^\circ$, $[R]_D^{25} 47.82$ (exaltation of +1.04 for two ethylenic linkings) (amide, m.p. 116—117°; anilide, m.p. 111—112°; *Me*, b.p. 113—114°/20 mm., 222°/760 mm., and *Et* ester, b.p. 228—229°/759 mm., 106—108°/7 mm.), and smaller amounts of three acids, (i) b.p. 139—141°/7 mm., (ii) m.p. 78—81°, and (iii) m.p. 103°. (I) and EtOH-Na (5 atoms) give dihydroshonanic acid (II), b.p. 142—143.5°/7 mm. (amide, m.p. 129—130°), hydrogenated (Pd) to tetrahydroshonanic acid, b.p. 142—143°/7 mm. (chloride, b.p. 115°/19 mm.; amide, m.p. 144°), which is also obtained by $\text{H}_2\text{-Pd-BaSO}_4$ from (I) and differs from dihydro- α -campholenic acid (prep. from camphor-oxime described). With hot 50% NaOH (I) is isomerised to isoshonanic acid, b.p. 151—152°/7 mm., 277—278°/756 mm., m.p. 45—46° (amide, m.p. 107—108°; chloride, b.p. 107—108°/20 mm.), which gives (II) with Na-EtOH . It is concluded that (I) contains two conjugated ethylenic linkings, of which one is semicyclic and becomes endocyclic on isomerisation.

R. S. C.

Homologues of the camphor group. XI. 4-Methyl-3-hydroxymethylenecamphor and its tautomersides. S. S. NAMETKIN and A. P. STUKOV. XII. Secondary 4-methyl- α -nitrocamphene and 4-methyl- α -camphenone. S. S. NAMETKIN and A. S. ZABRODINA (J. Gen. Chem. Russ., 1936, 6, 1659—1665, 1666—1668).—XI. 4-Methylcamphor and Na in Et_2O react with amyl formate at 0° to yield 4-methyl-3-hydroxymethylenecamphor, m.p. 117—120° (*Cu* salt; 3-benzoate, m.p. 101—101.5°; methyl-anilide, m.p. 90—91°), which gradually changes (67 days at room temp.) into 3-formyl-4-methylcamphor, m.p. 146—150°, reacts with Br to yield an unstable product, with NHPH-NH_2 to give a phenylpyrazolone derivative, m.p. 62—63°, and with semicarbazide to give a condensation product, m.p. 193—195° (decomp.).

XII. 4-Methylcycloene and HNO_3 yield 4-methyl- α -nitrocamphene, m.p. 40—40.5°, converted by KMnO_4 in aq. NaOH at 0° into 4-methyl- α -camphenone, m.p. 129—130° [semicarbazone, m.p. 211—212° (decomp.)].

R. T.

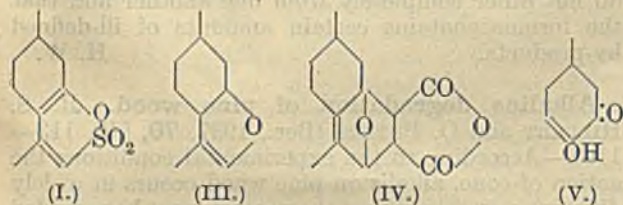
Identity of dacrene and sciadopitene with phyllocladene. L. H. BRIGGS (J.C.S., 1937, 79—80).—Phyllocladene (I), isolated from the leaf oils of *Phyllocladus alpinus* and *Araucaria excelsa*, is identical with dacrene, sciadopitene, and a diterpene from *Dacrydium cupressinum*. (I) is isomerised by H_2SO_4 - EtOH to isophyllocladene, which appears to be identical with the optical antipode of a diterpene from *Sciadopitis verticillata* (Kawamura, B., 1932, 321). (I) is hydrogenated to α - and β -dihydrophyllocladene.

F. R. S.

Caryophyllenes. V. Structure of homocaryophyllenic acid. G. R. RAMAGE and J. L. SIMONSEN (J.C.S., 1937, 73—75).—Oxidation of caryophyllene (HNO_3), followed by esterification (MeOH), gives Me dimethylsuccinate, Me norcaryophyllenate (I), and Me caryophyllenate. (I) is converted through the anhydride into the *cis*-ester, which with Na-EtOH , followed by PBr_3 , forms the Br_2 -compound. This substance with KCN followed by hydrolysis affords Me dl-2-carbomethoxymethyl-1:1-dimethylcyclobutane-3-acetate, b.p. 145—155°/19 mm., $\alpha_{\text{D}}^{25} +0.56^\circ$, which yields trans, m.p. 280°, and *cis*-dianilides, m.p. 170°. Reduction (Na-EtOH) of caryophyllenic anhydride yields a lactone, converted by KCN followed by MeOH-HCl into Me 2-carbomethoxy-1:1-dimethylcyclobutane-3- β -propionate, b.p. 145—146°/18 mm. (*dianilide*, m.p. 206°, $[\alpha]_{\text{D}}^{25} -28.3^\circ$ in $\text{C}_5\text{H}_5\text{N}$). Homocaryophyllenic acid (II) forms the Me ester, b.p. 145—147°/18 mm., $[\alpha]_{\text{D}}^{25} +56.9^\circ$, which gives a dianilide, m.p. 282°, and a *cis*-dianilide, m.p. 179°, $[\alpha]_{\text{D}}^{25} -57.5^\circ$ in CHCl_3 . The conclusion is reached that (II) is 2-carboxymethyl-1:1-dimethylcyclobutyl-3-acetic acid.

F. R. S.

Sulphonic acids of terpenes and sesquiterpenes. I. cyclopulegenolsulphonic ester and its transition into menthofuran. W. TREIBS (Ber., 1937, 70, [B], 85—89).—Gradual addition of pulegone to a well-cooled mixture of conc. H_2SO_4 and Ac_2O gives cyclopulegenolsulphonic ester (I), m.p. 85°, which is insol. in H_2O and cold alkalis and



converted by hot alkali or acid or superheated steam into a stable sulphonic acid, sol. in H_2O . Catalytic hydrogenation (Pd-MeOH) causes absorption of 4 H with production of a strongly acidic substance. (I) with KMnO_4 in COMe_2 affords β -methyladipic acid (II). (I) can be distilled unchanged under diminished pressure but when mixed with ZnO and heated under atm. pressure breaks down almost quantitatively into SO_2 and menthofuran (III), b.p. 80°/18 mm.,

$\alpha_{\text{D}} +92^\circ$, which is stable towards Na and absorbs 4 H when hydrogenated (Pd-sponge). Conjugation of the double linkings is established by the union of (III) with maleic anhydride in C_6H_6 to the adduct (IV), m.p. 138°, which absorbs 2 H when hydrogenated (Pd-sponge in COMe_2). Oxidation of (III) with KMnO_4 affords (II). (III) appears to be present in peppermint oil (Carles, B., 1930, 740) and to give rise to the characteristic blue colour when the oil becomes autoxidised. The "acid" $\text{C}_7\text{H}_{10}\text{O}_2$, m.p. 185—186°, obtained by its oxidation with CrO_3 is probably (V). (I) is well adapted to the identification of pulegone or isopulegone is fractions of essential oils.

H. W.

Structure of triterpenes. L. RUZICKA (Chem. & Ind., 1937, 119).—Concerning priority (Spring, this vol., 68; Ruzicka *et al.*, A., 1936, 607). R. S. C.

Lactucarium. II. G. SCHENCK and H. GRAF (Arch. Pharm., 1937, 275, 36—44; cf. A., III, 66).—Contrary to the experience of Ludwig *et al.* (1862) lactucin (0.32%) (I) was obtained from the H_2O -sol., and not from the H_2O -insol., part of commercial lactucarium, possibly owing to difference in the starting material; its occurrence in the degraded sample is unexpected. Inositol was also isolated. The coagulated fresh juice yields (I) (0.52%), $\text{C}_{15}\text{H}_{16}\text{O}_5$, m.p. 226° (decomp.), and another bitter substance (C 65.5, H 5.8%), m.p. 146° (decomp.) (from EtOH) (119° in the crude state, much influenced by atm. H_2O). The methods (for details see original) are not suited for general analysis.

R. S. C.

Glaucanin. V. Constitution of glauconic acid. K. KRAFT and H. PORSCH (Annalen, 1937, 527, 168—176).—The functions of the 6 O of glaucanin (I), $\text{C}_{11}\text{H}_8\text{O}_6$, are investigated. (I) is transformed by KOH and Me_2SO_4 into a Me_2 ester, $\text{C}_{13}\text{H}_{14}\text{O}_7$, m.p. 77°, formed by the entry of 1 mol. of H_2O . Two of the four acidic groups must be derived from an acid anhydride or enol-lactone group. Similar relationships are found in the treatment of the Ag_4 salt of (I) with EtI , whereby a non-cryst Et_2 ester is obtained which affords a 2:4-dinitrophenylhydrazones, $\text{C}_{21}\text{H}_{22}\text{O}_{10}\text{N}_4$, m.p. 153—154°. (I) does not give a colour with $\text{C}(\text{NO}_2)_4$ and behaves negatively towards BzO_2H although ozonisation establishes the presence of ≤ 2 double linkings. (I) is not hydrogenated (PtO_2) at room temp. and pressure but under more drastic conditions gives an acidic oil which after treatment with Me_2SO_4 contains 2 OMe and apparently 3 CO_2H when titrated in hot solution; the ester absorbs H_2 readily at room temp. and atm. pressure and the product behaves as a tribasic acid even after complete esterification with CH_3N_2 . It is therefore probable that (I) is an enol-lactone in which the acidic $\text{C}(\text{OH})$ disappears by addition of H_2O . This group and a neighbouring CO appear responsible for the dark blue colour given by (I) with $\text{C}_5\text{H}_5\text{N}$ and NH_3 . The two remaining acidic groups probably involve a disubstituted maleic anhydride arrangement, one half of the mol. being probably $\begin{array}{c} \text{C}-\text{CO} \\ \text{OMe}-\text{CO} \end{array} > \text{O}$. This view is supported by the production of 1.5 mols.

of AcOH when (I) is oxidised by CrO_3 . Enol-lactone and anhydride groups require 5 O and the remaining O is probably present as CO since (I) reacts with 2 mols. of NH_2OH [cf. valerolactone and coumarin do not react with NH_2OH , whilst $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ requires 1 NH_2OH]. The structure of (I) can therefore be partly resolved as in (A).

H. W.

Vegetable heart poisons. XIV. Ouabain. R. TSCHESCHE and W. HAUPT (Ber., 1937, 70, [B], 43—48).—The constitutional formula assigned to ouabain (I) by Fieser *et al.* (A., 1936, 1116) is exceptional in that it contains the sugar residue involving the *tert.* OH at C_{15} whereas in all other glucosides of this type the *sec.* OH at C_{13} is involved. The sole exception is furnished by scillaren, but its constitution is based on analogies and colour reactions of scillaridin. Comparison of the ultra-violet absorption spectrum of the latter with that of ergosterol suggests that in this case also the sugar residue is united to O attached to C_{13} , and that the ready elimination of OH from this group is due to the double linking between C_{15} and C_{14} . (I) is therefore considered to have the sugar residue attached to O at C_{13} . (I) is transformed into the α -lactone (II), $\text{C}_{22}\text{H}_{28}\text{O}_3$, m.p. 198—199° (Jacobs *et al.*, A., 1932, 856), accompanied by the β -lactone, $\text{C}_{22}\text{H}_{30}\text{O}_3$, m.p. 205—209°, $[\alpha]_D^{18} -85.42^\circ$ in CHCl_3 . (II) and the lactone $\text{C}_{22}\text{H}_{26}\text{O}_4$ (III) from isouabain have an absorption spectrum indicative of the presence of an aromatic system. On the basis of Fieser's formulation, ring A must be capable of becoming aromatic and (II) must be dehydrogenable in the same manner as neoergosterol (IV). The Me ether, m.p. 193—195°, is, however, stable under conditions which readily cause aromatisation of (IV). (IV) resembles *ac*-tetrahydro- β -naphthol in its inability to furnish a ketone when oxidised whereas the C-OH of (III) is readily transformed into CO. Fieser's assumption of the presence of OH in the β -position to an aromatic ring cannot therefore be correct if ring A is 6-membered. Fieser's structure of the lactones and conclusions as the positions of the OH groups in ouabagenin are therefore doubtful and all that can be stated at present is that 1 OH is attached to C_{14} of the cholane skeleton.

H. W.

Lignin and related compounds. XXVI. Properties of spruce lignin extracted with formic acid. G. F. WRIGHT and H. HIBBERT (J. Amer. Chem. Soc., 1937, 59, 125—130; cf. Freudenberg *et al.*, A., 1936, 995; Standinger and Dreher, *ibid.*, 1116).—Extraction of spruce-meal (free from resin and H_2O -sol. carbohydrates) with, *e.g.*, boiling 80% HCO_2H gives a lignin (I) (13.5% OMe), separable by successive extraction with CHCl_3 , COMe_2 , and aq. COMe_2 (and subsequent fractional pptn. from these extracts with Et_2O) into fractions (12.17—14.15% OMe). (I) contains 4 OH per kg. (Zerevitinov and triphenylmethylation) and adds a small but definite amount of MgRX (thus confirming the presence of CO, which does not exist as $\text{O}\cdot\text{COR}$). Methylation of (I) with CH_2N_2 indicates that 2 of the 4 OH are

phenolic. Methylation of (I) and the CHCl_3 - and COMe_2 -sol. fractions (OMe 13.13 and 12.81%, respectively, obtained from lignin extracted with 95% HCO_2H , and containing 4.6 and 3.5 OH, respectively) with Me_2SO_4 and aq. NaOH in N_2 gives products (24—27% OMe) which still contain 3—4 OH, indicating that new OH groups are produced during the methylation process; lignins isolated by other methods behave similarly. The no. of OH in an unfractionated HCO_2H -lignin is increased from 4 to 12.5 by treatment with 1% NaOH for 45 days (during which time no absorption of O_2 occurs). Alkaline methylation is thus untrustworthy as a means of determining lignin structure.

H. B.

Benzylated pine wood. R. S. HILPERT and O. PETERS (Ber., 1937, 70, [B], 108—113).—The reaction between CH_2PhCl , alkali, and pine wood appears to proceed very similarly to the corresponding reaction with cellulose and the composition of the product (I) lies within the limits established for benzylcellulose (II). The product can be separated by C_6H_6 -EtOH or AcOH into fractions of differing C content which in each case is within the limits for (II). Since (II) is sol. in C_6H_6 -EtOH its amount in (I) is ≈ 24 —30%. *Benzylalkali-lignin* (III) is sol. in warm $\text{CH}_2\text{Ph}\cdot\text{OH}$ or C_6H_6 , sparingly sol. in AcOH, whereas *benzylacid-lignin* (IV) dissolves with difficulty in all media and only very sparingly in C_6H_6 , $\text{CH}_2\text{Ph}\cdot\text{OH}$, or AcOH. When the relatively high C content of (III) and (IV) is also considered their presence in either component of (I) appears excluded. The components of (I) are therefore derived from a complex material and have their own sp. properties and not those of cellulose (V). Pine wood leaves about 45% of substance resembling (V) when heated with hot alkali, towards which its CH_2Ph ether is indifferent. Treatment with HCl removes about 33% of material from benzylated wood and the residue, which is partly sol. in MeOH, has neither the properties nor composition of (III) or (IV). The differing behaviour of untreated and treated wood is immediately comprehensible if it is assumed that the fission products are not components but reaction products the properties of which are modified immediately reactions are induced. (II) is dissolved by conc. HCl, leaving about 7% of residue. Protest is made against the view that alkali- and acid-lignin do not differ completely from one another and that the former contains certain amounts of ill-defined by-products.

H. W.

Alkaline degradation of pine wood. R. S. HILPERT and O. PETERS (Ber., 1937, 70, [B], 113—116).—According to the experimental conditions the action of conc. alkalis on pine wood occurs in widely differing manners so that the process must be regarded not as the dissolution of a portion of a heterogeneous material but as fission of a large complex. In the preformed condition cellulose and lignin are present to the extent of $< 45\%$ and $< 30\%$, respectively. Lignins containing OMe are produced by the action of acids on the methoxylated carbohydrates obtained as products of fission. It must therefore be assumed that lignin is formed similarly when wood is treated with acids.

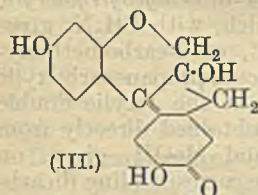
H. W.

isoPropylidene derivative, b.p. 193.5–194.5°/712 mm., of *as-furyl Me glycol*.—See A., III, 70.

Dihydro-1:4-pyrans. V. Structure of 3-cyano-derivatives. H. H. HULLY, F. H. BROCK, and R. C. FUSON (J. Amer. Chem. Soc., 1936, 58, 2634–2635).—3-Cyano-6-benzoyl-2-phenyl-5:6-dihydro-1:4-pyran (I) (A., 1932, 63) is reduced (H_2 , PtO_2 , $EtOAc$) to the 6- α -hydroxybenzyl derivative, m.p. 110–113° (*phenylcarbamate*, m.p. 137–138°), which is oxidised (CrO_3 , $AcOH$) to (I) and converted by fuming HNO_3 at 0° into 3-nitro-2-hydroxy-3-cyano-6-benzoyl-2-phenyltetrahydro-1:4-pyran 2-nitrate, m.p. 139.5–140° (decomp.), also obtained from (I) and HNO_3 (*d* 1.42) in $AcOH$ at 100°. Ozonolysis of (I) gives γ -benzoyloxy- γ -benzoylbutyric acid, m.p. 113° [*semicarbazone*, m.p. 190–195° (decomp.)], hydrolysed (aq. $NaOH$) to $BzOH$ and $(-CH_2CO_2H)_2$. These results support the structure previously assigned (*loc. cit.*) to (I). γ -Bromo- γ -benzoylbutyric acid and $AgOBz$ afford γ -benzoyl- γ -butyrolactone. H. B.

Synthesis of tangeritin. L. J. GOLDSWORTHY and R. ROBINSON (J.C.S., 1937, 46–49).—2:6-Dihydroxy- ω :3:4-trimethoxyacetophenone with anisic anhydride and Na anisate gives 5-hydroxy-3:6:7:4'-tetramethoxyflavone (I), m.p. 171°, methylated (Me_2SO_4) to 3:5:6:7:4'-pentamethoxyflavone, identical with tangeritin (cf. Nelson, A., 1934, 900). (I) is hydrolysed to the $(OH)_5$ -derivative, which has been characterised. F. R. S.

Constitution of brazilein. U. M. MIČOVIĆ and R. ROBINSON (J.C.S., 1937, 43–46).— ω -Homoveratrylresacetophenone (Na salt) and EtI give 2-hydroxy-4-ethoxyphenyl β -veratrylethyl ketone, m.p. 97–98°, which with HCO_2H and $ZnCl_2$, followed by $FeCl_3$, affords 4':5'-dimethoxy-7-ethoxybrazylum ferrichloride (I), m.p. 211–212° (decomp.). 7-Methoxychromanone and O -ethylisovanillin yield 7-methoxy-3-(4'-methoxy-3'-ethoxybenzylidene)chromanone, m.p. 120°, reduced ($Pd-H_2$) for a short period to a product, $C_{20}H_{22}O_5$, m.p. 83°, and for a longer period to the -ethoxybenzyl compound, m.p. 87–90°. This compound is dehydrated (P_2O_5) to deoxydimethylethylbrazilone, m.p. 145–147°, closely resembling deoxytrimethylbrazilone in all characteristic properties, and converted ($Br-FeCl_3$) into 7:5'-dimethoxy-4'-ethoxybrazylum ferrichloride (II). Trimethyl-dihydrobrazileinol, EtI , and K_2CO_3 give O -trimethylethyl-dihydrobrazileinol, m.p. 142°, resembling the Me_4 derivative. Dimethoxyethoxybrazylum ferrichloride, obtained from



brazilein (III) is identical with (II) and not (I). This confirms the view of the structure of (III).

F. R. S.

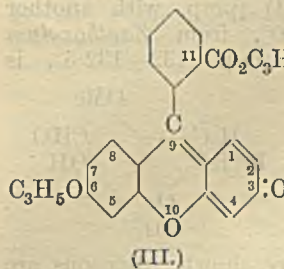
Synthesis of brazilin and hæmatoxylin. IV. Synthesis of O -diethylenehæmatoxylone. W. H. PERKIN, jun., A. POLLARD, and R. ROBINSON (J.C.S., 1937, 49–53).—2:3-Ethylenedioxy- β -phenoxypionic acid, m.p. 156.5–158°, prepared from 2:3-ethylenedioxyphenol and $CH_2Cl-CH_2-CO_2H$, with P_2O_5 affords 7:8-ethylenedioxychromanone, m.p. 120–121°. The chromanone condenses with 3:4-ethylenedioxy-

benzaldehyde to form 7:8:3':4'-bisethylenedioxy-3-benzylidenechromanone, m.p. 200–202°, converted by $FeCl_3-Ac_2O$ into 6:7:7':8'-bisethylenedioxy-chromeno(4':3':2:3)benzopyrylium ferrichloride, m.p. 232–233°, and reduced ($Pd-H_2$) to 7:8:3':4'-bisethylenedioxy-3-benzylchromanone, m.p. 130–132°. The benzylchromanone is dehydrated (P_2O_5) to O -diethylenedioxyhæmatoxylone (I). O -Diethylenehæmatoxylone, prepared from hæmatoxylone and $C_2H_4Br_2-K_2CO_3$, is oxidised (CrO_3) to O -diethylenehæmatoxylone, m.p. 198–200° (decomp.), reduced ($NHPh-NH_2$) to (I), m.p. 157°. F. R. S.

Constitution of catechin. M. NIERENSTEIN (Chem. and Ind., 1936, 1007–1008).—Isolation of pentamethyl-*dl*-epicatechin from the reduction products of pentamethylquercetin proves the correctness of Freudenberg's formula for catechin. J. W. B.

Synthesis of benzylidenephthalan. S. NATELSON and A. PEARL (J. Amer. Chem. Soc., 1936, 58, 2448–2449).—Phthalide (I) and $Et_2O-CH_2Ph-MgCl$ give 2-hydroxy-2-benzylphthalan, m.p. 137°, dehydrated by conc. H_2SO_4 at 40° or, better, by Se at 140° to benzylidenephthalan (II), $o-C_6H_4-\langle \begin{smallmatrix} C(CHPh) \\ CH_2 \end{smallmatrix} \rangle-O$, m.p. 94°, which is readily hydrolysed (acidic or basic reagents) to (I). (I), CH_2Ph-CO_2H (III), and small amounts of $NaOAc$ and pumice at 180° give $PhMe$ and (I); (III) does not evolve CO_2 under similar conditions, indicating that (II) is first produced and then hydrolysed. H. B.

Alkenyl derivatives of fluorescein. C. D. HURD and L. SCHMERLING (J. Amer. Chem. Soc., 1937, 59, 112–117).—The Na_2 salt of fluorescein [3:6-dihydroxyfluoran] (I) and allyl bromide (II) (2 mols.) in aq. $COMe_2$ give 43.5% of allyl 6-allyloxy-9-phenylfluorone-11-carboxylate (III), m.p. 155°, and 30% of 6-hydroxy-3-allyloxyfluoran (IV), m.p. 205° (acetate, m.p. 143°), whilst (I), (II), and K_2CO_3 in $COMe_2$ afford (III) (42%) and smaller amounts of 3:6-diallyloxyfluoran (V), m.p. 124°, and allyl 6-hydroxy-9-phenylfluorone-11-carboxylate [resorcinolbenzein-11-carboxylate], m.p. 233°. α -Bromo- Δ^8 -pentene and (I) similarly give γ -ethylallyl 6- γ -ethylallyloxy-9-phenylfluorone-11-carboxylate, m.p. 118°, 6-hydroxy-3- γ -ethylallyloxyfluoran (VI), m.p. 220° (acetate, m.p. 108°), and 3:6-di- γ -ethylallyloxyfluoran, m.p. 131°, whilst (I) and α -bromo- Δ^8 -hexene (VII) afford γ -*n*-propylallyl 6- γ -*n*-propylallyloxy-9-phenylfluorone-11-carboxylate, m.p. 109°, 6-hydroxy-3- γ -*n*-propylallyloxyfluoran, m.p. 187° (acetate, m.p. 154°), and 3:6-di- γ -*n*-propylallyloxyfluoran (VIII), m.p. 103°. (VIII) heated at 210–220° rearranges exothermally to 2:7-dihexenylfluorescein (IX), m.p. 135–140°. Ozonolysis of (VIII) gives much $PrCO_2H$ and some HCO_2H [indicating the presence of the α -propylallyl derivative and, hence, that (VII) contains γ -bromo- Δ^8 -hexene], whilst (IX) affords mainly HCO_2H (indicating inversion of the propylallyl group during rearrangement). (IV), (V), and (VI) are similarly



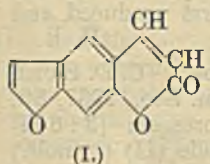
afford (III) (42%) and smaller amounts of 3:6-diallyloxyfluoran (V), m.p. 124°, and allyl 6-hydroxy-9-phenylfluorone-11-carboxylate [resorcinolbenzein-11-carboxylate], m.p. 233°. α -Bromo- Δ^8 -pentene and (I) similarly give γ -ethylallyl 6- γ -ethylallyloxy-9-phenylfluorone-11-carboxylate, m.p. 118°, 6-hydroxy-3- γ -ethylallyloxyfluoran (VI), m.p. 220° (acetate, m.p. 108°), and 3:6-di- γ -ethylallyloxyfluoran, m.p. 131°, whilst (I) and α -bromo- Δ^8 -hexene (VII) afford γ -*n*-propylallyl 6- γ -*n*-propylallyloxy-9-phenylfluorone-11-carboxylate, m.p. 109°, 6-hydroxy-3- γ -*n*-propylallyloxyfluoran, m.p. 187° (acetate, m.p. 154°), and 3:6-di- γ -*n*-propylallyloxyfluoran (VIII), m.p. 103°. (VIII) heated at 210–220° rearranges exothermally to 2:7-dihexenylfluorescein (IX), m.p. 135–140°. Ozonolysis of (VIII) gives much $PrCO_2H$ and some HCO_2H [indicating the presence of the α -propylallyl derivative and, hence, that (VII) contains γ -bromo- Δ^8 -hexene], whilst (IX) affords mainly HCO_2H (indicating inversion of the propylallyl group during rearrangement). (IV), (V), and (VI) are similarly

rearranged to 2-allyl-, m.p. 168—176°, 2:7-diallyl-, m.p. 158—161°, and 2-pentenyl-, m.p. 156—160°, -fluorescein, respectively; (III) gives allyl 2-allyl-resorcinolbenzein-11-carboxylate, m.p. 137—143°. Hydrolysis of (III) with aq. KOH affords (mainly) (I); NaOH in allyl alcohol or aq. COMe₂ gives (IV), whilst in MeOH and EtOH, fluorescein Me₂ (acetate, m.p. 141°) and Et₁ ether, respectively, result. Diacetylfuorescein is obtained from (I) and keten in COMe₂, whilst (I) and SOCl₂ give 3:6-dichlorofluoran, m.p. 262° (255° using PCl₅). *p*-Tolyl allyl and hexenyl, b.p. 142—146°/14 mm., ethers are readily obtained from *p*-C₆H₄Me-ONa and (II) and (VII), respectively, in aq. COMe₂ at room temp. H. B.

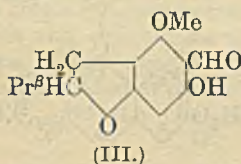
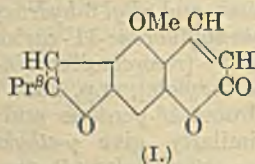
Resolution of diethylaminomethylbenzdioxan (883 F). TRÉFOUEL, J. TRÉFOUEL, and Y. DUNANT (Bull. Sci. Pharmacol., 1935, 42, 459—466; Chem. Zentr., 1936, i, 1220).—The *H* phthalate, m.p. 116°, of hydroxymethylbenzdioxan is converted into its *c*-ephedrine salt and resolved by fractionation with C₆H₆, yielding 1-hydroxymethylbenzdioxan, m.p. 81°, [α]_D²⁰—31° 40'; this, with SOCl₂, yields 1-chloromethylbenzdioxan, which with NHET₂ affords 1-diethylaminomethylbenzdioxan, b.p. 181°/38 mm., [α]_D²⁰—29° 10' (hydrochloride, m.p. 129—130°, [α]_D²⁰—58° 20').

H. N. R.

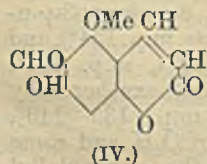
Identity of ficusin with psoralene. E. SPÄTH, K. OKAHARA, and F. KUFFNER (Ber., 1937, 70, [B], 731).—The identity of ficusin (Okahara, A., 1936, 1121), psoralene (Jois, A., 1933, 657), and the furocoumarin (I) (Späth *et al.*, A., 1936, 860) is established. The deletion of the term "ficusin" from the literature is suggested. H. W.



Constituent of *Zanthoxylum fraxineum*, Wild. H. DIETERLE and E. KRUTA [with, in part, W. SAUTER] (Arch. Pharm., 1937, 275, 45—53).—Xanthoxylin *N* (xanthoxyletin) (I) (prep. with another furocoumarin, m.p. 99—100°, from *Zanthoxylum fraxineum* bark described), m.p. 132—132.5°, is



proved to have the structure shown. Reasons are adduced against the alternative dicoumarin structure (cf. Bell *et al.*, A., 1936, 859). Hydrogenation (Pd-C) of (I) in EtOH at room temp./1 atm. gives dihydroxanthoxylin *N* (dihydroxanthoxyletin) (II), m.p. 145°, in which the coumarin ring remains unaffected, but with PdO₂ at 60—61°/6 atm. in AcOH gives tetrahydroxanthoxylin *N*, m.p. 134°. (I) and NaOEt-MeI give xanthoxylic-*N* acid Me ether (*O*-methylxanthoxyletin acid), C₁₆H₁₈O₅, m.p. 182—183°. (II) and O₃ in CHCl₃ yield the aldehyde (III), C₁₃H₁₆O₄, m.p. 86—87° (diminophenylhydrazone, m.p. 225°; Ac derivative, m.p. 116—117°). (I) and O₃ in CHCl₃ give 2:6-dialdehydophloglucinol 1-*O*-Me



ether, m.p. 165—166°, volatile in steam (obtained similarly from bergapten), and the substance (IV), C₁₁H₈O₅, m.p. 220—221°. (I) and 2% KMnO₄ give H₂C₂O₄ and OH-CMe₂-CO₂H. R. S. C.

Synthesis of diflavonols. J. ALGAR and (Miss) D. E. HURLEY (Proc. Roy. Irish Acad., 1936, 43, 83—87).—Oxidation (H₂O₂) of dichalkones in the cold yields the corresponding diflavonol and an unidentified product: from dibenzylidenediaceoresorcinol, diflavonol, m.p. 323° (diacetate, m.p. 252°), and a substance, m.p. 284°; from dianisylidenediaceoresorcinol, 4':4''-dimethoxydiflavonol, m.p. 306° (di-, m.p. 291°, and tetra-acetate, m.p. 270°), and a substance, m.p. 320—321° (Ac derivative, m.p. 263°); from dipiperonylidenediaceoresorcinol, 3':4':3'':4''-dimethylendioxymethoxydiflavonol, m.p. above 330° (diacetate, m.p. 291—292°), and a substance, m.p. above 330°; and from diveratrylidenediaceoresorcinol, 3':4':3'':4''-tetramethoxydiflavonol, m.p. 280°, and a substance, m.p. 315°. F. R. S.

Synthetic plant growth hormones. E. M. CROOK, W. DAVIES, and (Miss) N. E. SMITH (Nature, 1937, 139, 154—155).—Thionaphthen-2-acetic acid (I), m.p. 109° [synthesis: thionaphthen → 2-bromothionaphthen → thionaphthen-2-carboxyl chloride → (I)], has a much smaller growth activity (oat and pea tests) than might be expected from its similarity to 2-indolylacetic acid (II). An isomeride of (I), m.p. 141°, has approx. the same activity as (I) towards peas, but none towards oats. 1-Naphthylacetic acid is several times as active as (I) in both oat and pea tests. L. S. T.

Cleavage of azlactones by diazomethane and methyl alcohol and by alkoxides. Analogy to behaviour of chlorophyll and its derivatives. H. FISCHER and H. J. HOFMANN (Z. physiol. Chem., 1937, 245, 139—151).—The azlactone (I) of 5-aldehydro-2:4-dimethyl-3-ethylpyrrole in MeOH gives with CH₂N₂ a high yield of *Me* α-benzamido-β-2:4-dimethyl-3-ethylpyrrolacrylate (II), m.p. 220°. Similarly the azlactones of PhCHO and *p*-OAc-C₆H₄-CHO give the *Me* esters of the corresponding acrylic acids. The azlactone (III) of 3-aldehydro-5-carbethoxy-2:4-dimethylpyrrole in MeOH with 40% aq. KOH gives α-benzamido-β-5-carboxy-2:4-dimethylpyrrolacrylic acid, m.p. 210° (decomp.), which, with CH₂N₂ gives the *Me* ester (IV), m.p. 216°, of 5-carbomethoxy-2:4-dimethylpyrrolbenzamidocyclopropanecarboxylic acid, CH₂ having been added at the acrylic double linking. (IV), which is also obtained directly from the azlactone with CH₂N₂ and MeOH, gives, on hydrolysis with conc. alkali, the corresponding dicarboxylic acid, m.p. 176° (decomp.). The azlactone of 3-aldehydro-1-acetylinole in MeOH gives with CH₂N₂ the analogous *Me* ester, m.p. 243°, of acetylinolylbenzamidocyclopropanecarboxylic acid. (I) in abs. EtOH gives with Na or Pb-Na at >5° the *Et* ester, m.p. 215°, of α-benzamido-β-5-carbethoxy-2:4-dimethylpyrrolacrylic acid. The *Me* ester, m.p. 198°, of this acid is obtained from (I) in MeOH with Na at >10° and the *Me* ester, m.p. 220°, of the corresponding carbomethoxy-acid at 65°. (I) in hot PrOH and in hot isoamyl alcohol with Na gives the corresponding Pr₂, m.p. 202°, and diisoamyl ester, m.p. 168°.

Similarly (III) with MeOH and Na gives (IV) and with EtOH and Na the corresponding *Et* ester, m.p. 192°. Methylphosphoribide α in C_6H_5N with MeOH and Na gives the Me_3 ester of chlorin e_3 . 3-Thioaldehyde-5-carbethoxy-2:4-dimethylpyrrole with hippuric acid, Ac_2O , and $Cu(OAc)_2$ or PbO at 100° for 6 hr. gives the azlactone of 3-aldehyde-5-carbethoxy-2:4-dimethylpyrrole. W. McC.

Condensation of dimethylaniline with formaldehyde and piperidine. H. F. TSEU and Y. T. WANG (J. Chinese Chem. Soc., 1936, 4, 418—421).—Piperidine hydrochloride (I), CH_2O , $NPhMe_2$, and a few drops of piperidine in aq. EtOH give *N*-*p*-dimethylaminobenzylpiperidine, m.p. 43° (*auri*-, m.p. 120°, and *zinci*-chloride, m.p. 215°), and a little methylene-bis-piperidine (in strongly alkaline solution this is the main product). In strongly acid solution only di-(*p*-dimethylaminophenyl)methane is formed. No condensation occurred with NH_2Et_2 instead of (I) or with amides or $PhOMe$ instead of $NPhEt_2$. R. S. C.

Synthesis of 1-methyl-2-alkyl-(aryl- or aryl-alkyl)-3:4:5:6-tetrahydropyridines. Action of the Grignard reagent on amides. XI. R. LUKEŠ and O. GROSSMANN (Coll. Czech. Chem. Comm., 1936, 8, 533—542; cf. A., 1934, 902).—*N*-Methyl-2-piperidone (1 mol.) with $MgRI$ (3—4 mols.) free from RI in dry C_6H_6 affords 1-methyl-2:2-dialkylpiperidine, isolated as the perchlorate, and 1-methyl-2-alkyl-3:4:5:6-tetrahydropyridine, isolated as the picrate. The following are prepared: 1:2-dimethyl-, b.p. 40.5°/10 mm. [*perchlorate*, m.p. 228.5°; *picrate*, m.p. 156°; *aurichloride*, m.p. 169—170° (decomp.)]; *platinichloride*, m.p. 200° (decomp.), 1-methyl-2-ethyl-, b.p. 58°/10 mm. (*perchlorate*, m.p. 237°; *picrate*, an oil; *aurichloride*, m.p. 131°; *platinichloride*, m.p. 213°), -2-*n*-butyl-, b.p. 85°/12 mm. [*perchlorate*, m.p. 143°; *picrate*, m.p. 144°; *platinichloride*, m.p. 182° (decomp.)], -2-*n*-amyl-, b.p. 114.5°/10 mm. [*perchlorate*, m.p. 136°; *platinichloride*, m.p. 126° (decomp.)], -2-phenyl-, b.p. 136°/20 mm. (*perchlorate*, m.p. 146.5°; *picrate*, m.p. 133°), -2- α -naphthyl- (*perchlorate*, m.p. 135°; *picrate*, m.p. 140°), -2-benzyl-, b.p. 169°/25 mm. (*perchlorate*, m.p. 135°; *picrate*, m.p. 151°), and -2-phenylethyl-3:4:5:6-tetrahydropyridine, b.p. 168°/18 mm. (*perchlorate*, m.p. 105.2°; *picrate*, m.p. 105°); 1:2:2-trimethyl- [*picrate*, m.p. 270° (decomp.)], 1-methyl-2:2-diethyl-, b.p. 93°/16 mm. [*picrate*, m.p. 224° (decomp.)]; *platinichloride*, m.p. 233° (decomp.), and -2:2-dibutylpiperidine (*picrate*, m.p. 102°). J. L. D.

Dihydropyridine compounds. IV. 1-Phenyl- and 1-*p*-anisyl- α -dihydropyridine. P. KARRER, G. SCHWARZENBACH, and G. E. UTZINGER (Helv. Chim. Acta, 1937, 20, 72—79).—Reduction of 1-phenylpyridinium chloride (I) by Na-Hg in alkaline solution gives 1:1-diphenyltetrahydrodipyridyl and 1-phenyl-1:2-dihydropyridine (II), m.p. about 48—50°. (II) is strongly reducing and can be titrated potentiometrically with $K_3Fe(CN)_6$ in alkaline medium, whereby 2 eqvs. of the latter are used. The similarity of the reducing and optical properties of (II) with those of 1-methyl-1:2-dihydronicotinamide and 1-glucosido-1:2-dihydronicotinamide indicate the *ortho* structure of (II), which is confirmed by the

E^* (A., II.)

immediate formation of a resinous product from it and maleic anhydride in Et_2O or C_6H_6 , thus establishing the presence of conjugated double linkings. Reduction of (I) by Na-Hg in more strongly alkaline solution gives a substance, $C_{22}H_{17}ON_2$, m.p. 160° (decomp.). 2:4-Dinitrophenylpyridinium chloride is transformed by anisidine in EtOH into the *hydrochloride* of glutacondialdehydedianisidide, hydrolysed by boiling HCl to 1-*p*-anisylpyridinium chloride (III) (additive compound with $FeCl_3$). (III) is reduced by Na-Hg to 1-*p*-anisyl-1:2-dihydropyridine, m.p. 82°, which is stable only at a low temp. in an abs. vac. It immediately reduces cold $AgNO_3$ and indigotin-tetra-, tri-, and -di-sulphonate. Spectroscopically it is closely allied to (II). H. W.

Synthesis of pyrrolidines, piperidines, and hexahydroazepines [hexamethyleneimines]. J. H. PADEN and H. ADKINS (J. Amer. Chem. Soc., 1936, 58, 2487—2499).—Reduction [H_2 (200—400 atm.), Cu-Cr oxide, dioxan, 250—260°] of glutaramides gives 62—77% yields of piperidines and varying small amounts of other cleavage products; glutaripiperidines similarly afford the corresponding α -dipiperidino-pentanes. Thus, glutaramide gives piperidine (I); glutarphenylethylamide, m.p. 158.5—159.5°, affords 1-phenylethylpiperidine [*hydrochloride*, m.p. 232—233°; *picrate*, m.p. 147—148° (lit. 144—145°)], (I), mono- (II) and di- (III)-phenylethylamine, and $PhEt$; β -methylglutarphenylethylamide, m.p. 190—191.5°, yields 1-phenylethyl-4-methylpiperidine, b.p. 141—142°/12 mm. (*hydrochloride*, m.p. 254—256°), 4-methylpiperidine (*hydrochloride*, m.p. 186—189.5°), (II), and (III); β -phenylglutarphenylethylamide, m.p. 177.5—178°, furnishes 4-phenyl-1-phenylethylpiperidine, b.p. 170—174°/2 mm., m.p. 74—75° (*hydrochloride*, m.p. 270—271°), 4-phenylpiperidine (IV) (benzenesulphonyl derivative, m.p. 108—109°), (II), and (III); glutar-*n*-amylamide, m.p. 147—148°, gives 1-*n*-amylpiperidine (*hydrochloride*, m.p. 223—224°), and mono- and di- (V)-*n*-amylamine; β -methylglutar-*n*-amylamide, m.p. 149—150°, affords 4-methyl-1-*n*-amylpiperidine, b.p. 83—84°/10 mm. (*hydrochloride*, m.p. 239—241°), and (V); β -phenylglutar-*n*-amylamide, m.p. 166—167°, yields 4-phenyl-1-*n*-amylpiperidine, b.p. 129—130°/1 mm. (*hydrochloride*, m.p. 245—246°), (IV), and (V); $\beta\beta$ -dimethylglutar-*n*-amylamide, b.p. 210—212°/2 mm., m.p. 39—41°, furnishes 4:4-dimethyl-1-*n*-amylpiperidine, b.p. 96—97°/12 mm. (*hydrochloride*, m.p. 302°), and (V); β -phenylglutarbenzylamide, m.p. 159.5—160.5°, gives 4-phenyl-1-benzylpiperidine, b.p. 157—159°/1 mm. (*hydrochloride*, m.p. 212—213°), (IV), CH_2PhNH_2 , and $NH(CH_2Ph)_2$; glutaripiperidide, b.p. 193—197°/1 mm., m.p. 53—54°, affords α -dipiperidino-pentane (46%), b.p. 130—131°/2 mm. [*hydrochloride*, m.p. 252—253°; *picrate*, m.p. 188—189° (lit. 185°)], ϵ -piperidinoamyl alcohol (30%), and (I) (20%), whilst β -methyl-, b.p. 188—190°/1 mm., and $\beta\beta$ -dimethyl-, b.p. 183—187°/1 mm., -glutaripiperidides yield α -dipiperidino- γ -methyl- (71%), b.p. 123—125°/1 mm. (*hydrochloride*, m.p. 246—248°), and - $\gamma\gamma$ -dimethyl-pentane (45%), b.p. 133—134°/1 mm. (*hydrochloride*, m.p. 314—316°), respectively. Glutarimides are similarly reduced to piperidines but fission of, e.g., $>NCH_2Ph$ is appreciable: thus,

$\beta\beta$ -dimethylglutar-N-n-*amyl*-, b.p. 115–116°/2 mm., -*benzyl*-, b.p. 148–151°/2 mm., m.p. 63–64°, and -*phenylethyl*-, m.p. 80.5–81.5°, -*imides* give 1-n-*amyl*-, b.p. 96–97°/12 mm. (*hydrochloride*, m.p. 302°), 1-*benzyl*-, b.p. 114–115°/5 mm. (*hydrochloride*, m.p. 335–336°), and 1-*phenylethyl*-, b.p. 149–150°/12 mm. (*hydrochloride*, m.p. 252°), -4:4-dimethylpiperidine, respectively, together with 7–31% of 4:4-dimethylpiperidine; β -phenylglutar-N-*benzylimide*, m.p. 98–99°, affords 4-phenyl-1-*benzylpiperidine* (42%) and (IV) (32%), whilst β -methyl- and β -phenyl-glutarimide yield 4-methylpiperidine (46%) and (IV) (55%), respectively. 1-Substituted piperidines and pyrrolidines are also obtained when equimol. mixtures of NH_2R with, e.g., pentane- $\alpha\epsilon$ - (VI) and butane- $\alpha\delta$ -diol (VII), respectively, are subjected to hydrogenolysis under the above conditions; the method is probably the most convenient of those studied. Thus, 1-*benzyl*- (71%) and 1-*phenylethyl*-piperidine (76%) are formed from (VI) with $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ and phenylethylamine, respectively; the use of (VII) gives 1-*benzyl*- (*hydrochloride*, m.p. 153.5–154.5°) and 1-*phenylethyl*-pyrrolidine [under milder conditions δ -phenylethylaminobutyl alcohol, b.p. 176–178°/9 mm. (*hydrochloride*, m.p. 127–128°); O-Bz derivative *hydrochloride*, m.p. 153–155°, is also produced]. γ -Methylpentane- $\alpha\epsilon$ -diol + $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ afford (mainly) 1-*benzyl*-4-methylpiperidine, b.p. 128–129°/14 mm. (*hydrochloride*, m.p. 166.5–168°); γ -phenylpentane- $\alpha\epsilon$ -diol + *n*-amylamine yield (mainly) 4-phenyl-1-n-*amylpiperidine*, whilst hexane- $\alpha\epsilon$ -diol + $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ give 23% of 1-*benzyl*-hexahydroazepine [*azacycloheptane*], b.p. 130–132°/12 mm. (*hydrochloride*, m.p. 158.5–159.5°), which is cleaved by H_2 + Cu-Cr oxide at 275° to $[\text{CH}_2]_6\text{NH}$ and PhMe.

Adip-n-*amylamide* is reduced (as for other amides) to 1-n-*amyl*hexahydroazepine (34%), b.p. 94–95°/13 mm. (*hydrochloride*, m.p. 217–218°; *picrate*, m.p. 109–110°), and (V) (41%). Similarly, 1-n-*amyl*- (VIII), b.p. 87–88.5°/1 mm., and 1- β -cyclohexylethyl- (IX), b.p. 136–138°/2.5 mm., -2-pyrrolidone give 1-n-*amyl*- (87%) and 1- β -cyclohexylethyl- (96%), b.p. 116–117°/12 mm. (*hydrochloride*, m.p. 224–225°), -pyrrolidine, respectively, whilst 1- β -cyclohexylethyl-4-methyl-2-piperidone (X), b.p. 146–149°/2 mm., affords 1- β -cyclohexylethyl-4-methylpiperidine (89%), b.p. 135.5–137°/12 mm. (*hydrochloride*, m.p. 277–278°). 2-Pyrrolidones and 2-piperidones are obtained from succin- and glutar-imides, respectively, by hydrogenolysis over Ni at 200–220° in dioxan. Thus, succin-N- β -phenylethylimide yields the cyclohexylethylimide, b.p. 145–148°/2 mm., m.p. 53–54°, and thence (IX); (VIII) and (X) are prepared from succin-N-n-*amylimide* and β -methylglutar-N- β -phenylethylimide, m.p. 98–100°, respectively. 2-Methyl-1-n-*amylpiperidine*, b.p. 92–93°/16 mm. (*hydrochloride*, m.p. 166.5–167.5°) (by amination of the 2-Me derivative), glutar-N-n-*amylimide*, b.p. 105–106°/1 mm., β -methylglutarbenzylamide, m.p. 194–195°, and β -phenylglutarpiperidide, b.p. 240–248°/1 mm., are described.

The amides of glutaric and β -methyl- and β -phenylglutaric acids are prepared from the Et esters and the appropriate amine (4 mols.) at 175–250° under 100–150 atm. of H_2 (Et $\beta\beta$ -dimethylglutarate similarly

gives amide + imide); the imides are formed from the acids and amine (1 mol.) at 250°. An improved prep. of Et glutarate is given. H. B.

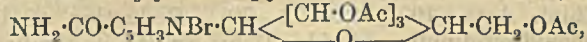
Products of the coupling of diazo-compounds with phenacylpyridinium salts. F. KROLLPFETTER and E. BRAUN (Ber., 1937, 70, [B], 89–95).—Phenacylpyridinium bromide with PhN_2HSO_4 in presence of NaOAc gives a mixture of benzeneazo-phenacylpyridinium bromide, decomp. 215° (corresponding chloride, decomp. about 185°) (the nomenclature is provisional), and benzeneazo-

$\text{C}_5\text{H}_5\text{N}^+(\text{+})$
 $\text{ArC}\cdot\text{C}\cdot\text{N}\cdot\text{NAr}$
 $\text{O}(-)$
 (A.)

phenacylpyridiniumbetaine (I) (cf. A), decomp. 120°; in absence of NaOAc (I) is the sole product. p-Nitrobenzeneazo-phenacylpyridinium bromide, decomp.

230–235° according to the rate of heating, the corresponding chloride, decomp. about 255°, and the betaine (II), decomp. 155–156°, are obtained analogously. Benzeneazoacetylpyridinium chloride, decomp. 180°, and the corresponding betaine (III), decomp. 100°, are identical with the products obtained from $\text{C}_5\text{H}_5\text{N}$ and α -chloropyruvaldehyde- α -phenylhydrazone. ω -Methylphenacylpyridinium bromide gives only resinous products. When heated (I) loses $\text{C}_5\text{H}_5\text{N}$ and gives the reddish-brown substance (IV), $\text{C}_{28}\text{H}_{20}\text{O}_2\text{N}_4$, m.p. 200–201° (probable constitution in accordance with $\text{NPh}\langle\text{C}\cdot\text{C}\cdot\text{N}\rangle\text{NPh}$ or $\text{C}\cdot\text{C}\cdot\text{N}\langle\text{C}\cdot\text{C}\cdot\text{N}\rangle\text{NPh}$), also obtained by protracted boiling of (I) with MeOH and converted by conc. HNO_3 in AcOH into the $(\text{NO}_2)_2$ -compound (I), m.p. 251–252° (decomp.), identical with that derived from (II). o- and m-Nitrobenzeneazophenacylpyridiniumbetaine yield compounds, $\text{C}_{28}\text{H}_{18}\text{O}_6\text{N}_6$, decomp. 224–225° and 179–180°, respectively. The product from (III) is identical with that obtained by use of boiling EtOH. (IV) is transformed by short treatment with NaOEt in boiling EtOH into a colourless substance, $\text{C}_{14}\text{H}_{12}\text{N}_4$, m.p. 111–112°. Similar treatment of (V) affords BzOH, an acid, m.p. 164–165° and m.p. >335° after re-solidification (Na salt), and a substance, m.p. 214–215°. Phenacylpyridinium bromide phenylhydrazone is converted by NaOEt-EtOH into $\text{C}_5\text{H}_5\text{N}$ and a substance, decomp. 135–136°, converted by 48% HBr into a compound, m.p. 113–114°. H. W.

Model experiments on the groups of the co-enzymes concerned with hydrogen transference. P. KARRER, B. H. RINGIER, J. BÜCHI, H. FRITZSCHE, and U. SOLMSEN (Helv. Chim. Acta, 1937, 20, 55–71).—Nicotinamide (I), m.p. 131–132° (improved prep. from Et nicotinate), is transformed by acetobromoglucose in dioxan at 35° into 3-carbamyl-1-tetra-acetylglucosidopyridinium bromide (II),



decomp. 192–200°, which, like cozymase and the H-carrying co-enzyme, reduces Fehling's solution. Reduction of (II) by $\text{Na}_2\text{S}_2\text{O}_4$ in presence of NaHCO_3 causes absorption of 2 H with production of a dark yellow solution and formation of 1-tetra-acetylglucosido-1:2(or 1:6)-dihydronicotinamide (III), m.p. 157–158°, hydrolysed by NH_3 -EtOH to 1-d-glucosido-1:2(or 1:6)-dihydronicotinamide (IV), decomp. 203–205°, the structure of which is established

by comparison with 1-methyl-*o*-dihydronicotinamide (V) and the reduced co-enzyme. The spectroscopic behaviour of (III) and (IV) is identical with that of the reduced form of the co-enzyme. The reducing power of (IV) is \ll that of (V); it reduces cold AgNO_3 (without NH_3) very slowly, rapidly when heated. $\text{K}_3\text{Fe}(\text{CN})_6$ does not dehydrogenate it in alkaline solution. It appears stable towards atm. O_2 , but is readily oxidised thereby in the presence of flavin. 1 mol. of (IV) absorbs 1 O_2 , and since H_2O_2 does not appear to be isolable it is probably destroyed by secondary changes. (III) is hydrolysed to (I) by prolonged contact with hot, very dil. H_2SO_4 . Therefore (IV) is probably the analogue of the reduced forms of the H-transferring groups of co-enzymes from which it differs in the nature of the sugar group and the absence of the phosphate residue. (I) and acetobromoarabinose in dioxan give non-cryst. 3-carbamyl-1-triacetyl-arabinosidopyridinium bromide, reduced to the non-cryst. H_2 -derivative, which is hydrolysed to 1-arabinosido-1:2(or 1:6)-dihydronicotinamide (VI); a similar sequence of changes leads to 1-xylosido-1:2(1:6)-dihydronicotinamide (VII), which, like (VI), closely resembles (IV) in reducing power and spectroscopic behaviour. 1-d-Tetra-acetylglucosidopyridinium bromide is reduced by $\text{Na}_2\text{S}_2\text{O}_4\text{-NaHCO}_3$ to 1-d-tetra-acetylglucosido-1:2-dihydropyridine, m.p. 154—155°, hydrolysed to 1-d-glucosido-1:2-dihydropyridine; both compounds reduce warm AgNO_3 and are stable to $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution; nicotinonitrile gives 3-cyano-1-d-tetra-acetylglucosidopyridinium bromide, m.p. 156°, which absorbs 2 H but appears also to undergo secondary change during the process. 3-Carboethoxy-1-d-tetra-acetylglucosidopyridinium bromide (non-cryst.) is smoothly reduced by $\text{Na}_2\text{S}_2\text{O}_4\text{-NaHCO}_3$ to Et 1-d-tetra-acetylglucosido-1:2-dihydropyridine-3-carboxylate, m.p. 146.5°. (IV), (VI), or (VII) cannot replace cozymase in fermentation experiments.

H. W.

Action of thionyl chloride on 2-methylpyridinecarboxylic acids and 2:6-lutidine. New type of oxidation reaction of thionyl chloride. R. GRAF and F. ZETTL (J. pr. Chem., 1936, [ii], 147, 188—198; cf. A., 1932, 401).—6-Methylnicotinic acid (I) when warmed with SOCl_2 gives its acid chloride hydrochloride, decomp. about 120°, but when heated (closed vessel; 120°; 6 hr.) and then treated with MeOH gives Me 6-(trichloromethyl)nicotinate (II), m.p. 82—84°, and some Me₂ isocinchomeronate. The latter, however, is the chief product when (I) and SOCl_2 are boiled (15 hr.) and then treated with MeOH. Gentle hydrolysis of (II) gives 6-(trichloromethyl)nicotinic acid, m.p. 183—184° (Ph ester, m.p. 87—89°), which with HI gives (I) and with boiling 80% H_2SO_4 gives isocinchomeric acid. 6-Methylpicolinic acid (III) when warmed with SOCl_2 gives its acid chloride hydrochloride (IV), m.p. 120° (decomp.), whilst when heated (closed vessel; 180°; 10 hr.) or boiled with SOCl_2 for a long time, and then treated with MeOH it gives Me 6-(trichloromethyl)picolinate (V), m.p. 108—110°, and Me₂ dipicolinate (VI). The former on gentle hydrolysis gives 6-(trichloromethyl)picolinic acid, m.p. 140—143° (amide, m.p. 119—122°), hydrolysed by 80% H_2SO_4 to pyridine-

2:6-dicarboxylic acid. The compound, m.p. 195°, obtained by Turnau (A., 1905, i, 546) from (III) is probably a mixture of (IV) and the hydrochloride of (III). By similar methods 6-methylpyridine-2:4-dicarboxylic acid yields Me₃ pyridine-2:4:6-tricarboxylate, m.p. 150—152°, and Me₂ 6-(trichloromethyl)pyridine-2:4-dicarboxylate, m.p. 114—116°. 2:6-Lutidine hydrochloride when heated (closed vessel; 180°; 20 hr.) with SOCl_2 yields 2:6-di(trichloromethyl)pyridine, m.p. 86—87°, hydrolysed according to conditions by $\text{H}_2\text{SO}_4\text{-MeOH}$ to (V) or (VI).

H. G. M.

5:7-Dimethyloxindole. V. LIVOVSKII (Compt. rend., 1936, 203, 1265—1267; cf. A., 1935, 1131).—*p*-Xylidine with $\text{CH}_2\text{Cl}\cdot\text{COCl}$ affords a compound, cyclised (AlCl_3) to 5:7-dimethyloxindole (I), m.p. 153°, which with the appropriate aromatic aldehyde (equimol. amount) in hot EtOH containing piperidine gives 3-benzylidene- (II), m.p. 195°, 3-*p*-chlorobenzylidene-, m.p. 167°, 3-piperonylidene-, m.p. 198°, 3-furfurylidene-, m.p. 246°, and the Na salt, decomp. at 285°, of 3-*o*-sulphobenzylidene-5:7-dimethyloxindole. (I) with excess of PhCHO affords, besides (II), 3:3'-benzylidenedi-5:7-dimethyloxindole, m.p. 175°, and with isatin in AcOH-HCl it affords 5:7-dimethylisindigotin (III), decomp. >360°, whereas in Et₂O-piperidine, 5:7-dimethylisatin results, which is converted into (III) at 185—190°. (I) with isatin chloride in anhyd. C_6H_6 affords 5:7-dimethylindirubin (A., 1919, i, 457) which dyes wool violet. (I) with isoamyl nitrite similarly affords 5:7-dimethylisatin oxime, m.p. 223° (decomp.).

J. L. D.

Isatincarboxylic acids. H. WALDMANN (J. pr. Chem., 1937, [ii], 147, 338—343).—*o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ is converted by $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$, $(\text{NH}_2\text{OH})_2$, H_2SO_4 , and H_2SO_4 in boiling H_2O into Me oximinoacetanilic acid (I), m.p. 180°. *p*-Oximinoacetamidobenzoic acid, m.p. >310°, its Me ester (II), m.p. 231°, and *m*-oximinoacetamidobenzoic acid (III), m.p. 228°, are obtained similarly. Gradual addition of (I) to conc. H_2SO_4 at 70—75° affords Me isatin-7-carboxylate, m.p. 192°, hydrolysed to isatin-7-carboxylic acid, m.p. 276—277°, which with COPhMe, EtOH, and 33% KOH gives 2-phenylquinoline-4:8-dicarboxylic acid, m.p. >310°. (II) is transformed similarly into isatin-5-carboxylic acid, m.p. 292—293° (decomp.) (oxime, decomp. 282°; Me ester, m.p. 264°, and its oxime, decomp. 280°), whence 2-phenylquinoline-4:6-dicarboxylic acid, m.p. >310°. (III) yields isatin-6-carboxylic acid, m.p. 292° (decomp.) (Me ester, m.p. 209°).

H. W.

Salts of phosphotungstic and metatungstic acids with organic bases. E. A. NIKITINA (J. Gen. Chem. Russ., 1936, 6, 1624—1631).—The salts R_6HX , $\text{R}'_4\text{H}_3\text{X}$, $\text{R}''_2\text{X}$, $\text{R}_7\text{H}_3\text{X}'$, $\text{R}_6\text{H}_4\text{X}'$, and $\text{R}''_7\text{H}_3\text{X}'\cdot x\text{H}_2\text{O}$ (R = quinoline, R' = $\text{C}_5\text{H}_5\text{N}$, R'' = NH_2Et , X = $[\text{P}(\text{W}_2\text{O}_7)]_6$, X' = $[\text{H}_2(\text{W}_2\text{O}_7)]_6$) are described. The solubility of the salts in 14% HCl at 0—100° is determined; R_6HX and $\text{R}_7\text{H}_3\text{X}'$ are insol.

R. T.

Bromo-derivatives of *N*-allylquinolinium salts. C. CANDEA, E. MACOVSKI, and J. KUHN (Atti V Congr. Naz. Chim., 1936, 1, 330—336).—*N*-Allylquinolinium bromide, m.p. 171°, in MeOH with Br

gives successively *N*- β -*γ*-dibromopropylquinolinium bromide, m.p. 192° (decomp.), and dibromobromide, m.p. 107—108°. The former with KI yields *N*- β -*γ*-dibromopropylquinolinium iodide, m.p. 136—137°, which with Br gives the dibromiodide, m.p. 123°; the last is the only product when *N*-allylquinolinium iodide is treated in MeOH with 2 or 4 Br.

E. W. W.

Derivatives of methylcarbostyryl. H. WALDMANN (J. pr. Chem., 1937, [ii], 147, 321—325).—4-Hydroxy-1-methylcarbostyryl (I), m.p. 264.5°, readily obtained from boiling $\text{CH}_2(\text{CO}_2\text{Et})_2$ and NHPhMe , couples with *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ to 3-*m*-nitrobenzene-azo-4-hydroxy-1-methylcarbostyryl (II), m.p. 210—211°, transformed by SnCl_2 and boiling HCl into 3:4-dihydroxy-1-methylcarbostyryl, m.p. 234—235° (decomp.) (Ac_2 derivative, m.p. 185—186°). Reduction of (II) by $\text{Na}_2\text{S}_2\text{O}_4$ and alkali affords 3-amino-4-hydroxy-1-methylcarbostyryl (III), m.p. 253° (3-*Ac* derivative, m.p. 196°). Successive treatment of (III) with H_2SO_4 — KNO_2 , SnCl_2 —HCl, and CaSO_4 leads to 2:4-diketo-1-methyl-1:2:3:4-tetrahydroquinoline-3-hydrazone, m.p. 166—167°, converted by NaOEt in abs. EtOH into (I).

H. W.

Preparation of 2-hydroxy-4-methylquinolines. (SIGNA.) L. MONTI and (SIGNA.) V. CIRELLI (Gazzetta, 1936, 66, 723—731).—The effect of substituents (Cl, Br, Me, OMe, NO_2 , and Ac) on the condensation of anilines with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and on the dehydration of the product to a 2-hydroxy-4-methylquinoline is studied. *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ does not condense; the products from *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and *p*- $\text{C}_6\text{H}_4\cdot\text{Ac}\cdot\text{NH}_2$ do not yield the quinoline. *m*-Bromoacetoacetanilide, new m.p. 108—110°, gives 7-bromo-2-hydroxy-4-methylquinoline, m.p. 286—288°. *p*-Chloro- and *p*-bromo-acetoacetanilide form respectively 6-chloro-, m.p. 292—294°, and 6-bromo-2-hydroxy-4-methylquinoline, m.p. 292—293°. *m*-Acetoacetanilide, m.p. 96—98°, is not dehydrated by H_2SO_4 ; in heavy petroleum at 300° it gives a substance, m.p. 230° (decomp.).

E. W. W.

Action of formaldehyde on hydroxyquinolines. (SIGNA.) L. MONTI (Atti V Congr. Naz. Chim., 1936, 1, 403—407).—6-Hydroxyquinoline and CH_2O in alkaline solution yield bis-[6-hydroxy-5(or 7)-quinolyl]-methane, but in H_2SO_4 6-hydroxy-5(or 7)-quinolyl-carbinol cyclomethylene ether is formed. 4-Hydroxy-2-alkyl- or -aryl-quinolines give 4-hydroxy-2-alkyl- or -aryl-3-quinolylcarbinol cyclomethylene ethers.

E. W. W.

Action of formaldehyde on hydroxyquinolines. II. (SIGNA.) L. MONTI and D. DINELLI (Gazzetta, 1936, 66, 732—734; cf. A., 1936, 617).—2-Hydroxy-4:6-dimethyl- and 6-chloro-2-hydroxy-4-methylquinoline in H_2SO_4 with 40% CH_2O give respectively 2-hydroxy-4:6-dimethyl-, m.p. 137—138° (picrate, m.p. 187°), and 6-chloro-2-hydroxy-4-methyl-3-quinolylcarbinol cyclomethylene ether, m.p. 169—171° (picrate, m.p. 187—189°).

E. W. W.

Synthesis of phenanthridine derivatives by an application of the Stieglitz rearrangement. L. A. PINCK and G. E. HILBERT (J. Amer. Chem. Soc., 1937, 59, 8—13).—9-Chloro-9-phenylfluorene (I) and liquid NH_3 at 60° (sealed tube) give 9-amino-9-

phenylfluorene, m.p. 82° [hydrochloride, m.p. 310° (decomp.)]; *Ac*, m.p. 232°, *N*-*Br*-, m.p. 105° (decomp.), *N*-*Cl*- (II), m.p. 102°, and *NN*-*Cl*-, m.p. 150° (decomp.), derivatives]; with dry NH_3 at 180° some *di*-(9-phenyl-9-fluoryl)amine, m.p. 230°, is also produced. 9-Chloro-9- α -naphthylfluorene with dry NH_3 at 80° and $\text{MeCN}\cdot\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (excess) affords 9-amino-9- α -naphthylfluorene, m.p. 186° [hydrochloride, m.p. 271° (decomp.)]; *N*-*Cl*-derivative (III), m.p. 133—135° (decomp.), and 9- α -naphthyl-9-fluorylhydrazine, m.p. 98° (decomp.) (previous sintering) [hydrochloride, m.p. 217° (decomp.)]; corresponding azide (IV), m.p. 133°, respectively. 9-Bromo-9-methylfluorene and liquid NH_3 in PhMe at 75° give 9-amino-9-methylfluorene (V), m.p. 96° [hydrochloride, m.p. 266° (decomp.)], 9-fluorylmethylamine (?), m.p. 99—100° [hydrochloride, m.p. 294° (decomp.)], *di*-(9-methyl-9-fluoryl)amine, m.p. 166° [hydrochloride, m.p. 263—265° (decomp.)], and an appreciable amount of polymeric diphenylene-ethylene. (II), (III), and the unstable *N*-*Cl*-derivative of (V), which are prepared from the amine hydrochlorides and cold aq. KOCl in EtOH, are converted by NaOMe in $\text{C}_2\text{H}_5\text{N}$ into 9-phenyl- [hydrochloride, m.p. 226° (lit. 220°)], 9- α -naphthyl- (VI), m.p. 123.5° [hydrochloride, m.p. 224° (decomp.)]; picrate, m.p. 251°, and 9-methyl-phenanthridine [picrate, m.p. 250° (decomp.) (lit. 233°)], respectively. (VI) is also formed when (IV) is heated at 194°. The primary factor controlling the rearrangement of the intermediate free radical from these *N*-*Cl*-derivatives is considered to be the strained condition of the five-membered ring. 9-Hydroxy-9- α -naphthylfluorene and fluorenone form a mol. compound, m.p. 109—110°. All m.p. are corr.

H. B.

Meso-derivatives of acridine. VI. Derivatives of 5-aminoacridine and 5-(dimethylaminophenyl)acridine. N. S. DROZDOV (J. Gen. Chem. Russ., 1936, 6, 1641—1650).—5-Chloro-3-methylacridine and PhOH (100°; 30 min.) yield 10-phenoxy-2-methylacridine (I), m.p. 133—134°, which, when heated at 120° for 2 hr. with PhOH and $\text{NHMe}_2\cdot\text{HCl}$, affords 5-dimethylamino-3-methylacridine, m.p. 251—252° (hydrochloride, m.p. >300°). (I) affords 5-(*p*-arsinoanilino)-3-methylacridine, m.p. 268—269°, when fused with PhOH and arsanilic acid (II), and 3-methylacridine-5-glycine, m.p. 226—228° (decomp.), with glycine and PhOH. 3-Methylacridine, NPhMe_2 , and POCl_3 (100°; 2 hr.) give 5-(dimethylaminophenyl)-3-methylacridine, m.p. 231—232°. 5-Phenoxyacridine and (II) in PhOH at 100° yield 5-(*p*-arsinoanilino)-acridine, m.p. 264—265°. 5-Phenoxy-3-methoxyacridine similarly gives 5-dimethylamino-, m.p. 275—276°, and 5-(*p*-arsinoanilino)-acridine, m.p. 245—248°, and 3-methoxyacridine-5-glycine, m.p. 230—231° (decomp.). *o*-Chlorobenzoic acid, (II), K_2CO_3 , glycerol, and Cu at 120—130° (3 hr.) yield 4'-arsinodiphenylamine-2-carboxylic acid, m.p. 278° (decomp.), converted by H_2SO_4 (100°; 1 hr.) into acridone-3-arsinic acid, m.p. >300°, and this condenses with NPhMe_2 in presence of POCl_3 to yield 5-(dimethylaminophenyl)acridine-3-arsinic acid, m.p. 230—232°. (I) does not react with *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ under the above conditions.

R. T.

Manufacture of salts of acridinium bases.—See B., 1937, 23.

[Acridones.] K. LEHMSTEDT (Ber., 1937, 70, [B], 172—173).—A reply to Tănăsescu *et al.* (A., 1936, 1520). H. W.

K salt of 4-nitrosopyrazolone-3-carboxylic acid.—See A., III, 60.

Reaction between Schiff's bases and pyrazolone derivatives. M. PASSERINI and G. RAGNI [with G. CUSMANO] (Gazzetta, 1936, 66, 684—688).—Benzylidene-aniline and -*p*-toluidine condense slowly with antipyrine in EtOH to 4- α -anilino-, m.p. 185—187°, and 4- α -*p*-toluidino-benzyl-2:3-dimethyl-5-pyrazolone, m.p. 184—186°, respectively, both hydrolysed to benzylidenebisantipyrine. Either reagent gives directly benzylidenebis-(1-phenyl-3-methyl-5-pyrazolone) when treated in cold EtOH with 1-phenyl-3-methyl-5-pyrazolone; with anisylideneaniline the last forms the corresponding anisylidene derivative.

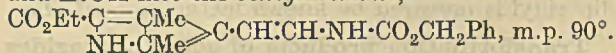
E. W. W.

Histamine formation from histidine through ascorbic acid. P. HOLTZ (Naturwiss., 1937, 25, 14).—Histidine in neutral aq. solution containing ascorbic acid is converted into histamine (blood-pressure test) by O₂ but not by N₂ (cf. A., 1936, 885).

J. L. D.

Synthesis of benzoylpyrromethenes. H. FISCHER and J. HEIDELMANN (Annalen, 1937, 527, 115—138).—3-Benzoyl-4-phenyl-2-methylpyrrole (I) is readily condensed by 100% HCO₂H and 48% HBr to 4:4'-dibenzoyl-3:3'-diphenyl-5:5'-dimethylpyrromethene (II), m.p. 212° (hydrobromide, m.p. 242°; picrate, m.p. 215°), also formed when (I) is condensed with Et 3-aldehydo-2:4-dimethylpyrrole-5-carboxylate (III). Analogously (I) does not react with 5-aldehydo-2:3:4-trimethylpyrrole or 2:4-dimethyl-3-ethylpyrrole (IV), which afford 3:4:5:3':4':5'-hexamethylpyrromethene, m.p. 295°, and 3:3':5:5'-tetramethyl-4:4'-diethylpyrromethene, m.p. 243°, respectively. (I) in Et₂O is transformed by HCN-HCl into the imine hydrochloride and thence into 3-benzoyl-4-phenyl-2-methylpyrrole-5-aldehyde (V), m.p. 156° (phenylhydrazone, m.p. 114°). 3-Benzoyl-2:4-dimethylpyrrole-5-aldehyde (VI), m.p. 170° (phenylhydrazone, m.p. 168°; semicarbazone, m.p. 215°; aldazine, C₂₈H₂₆O₂N₄, m.p. 279°), is obtained similarly, (I) and (V) readily afford (II). With 2:3:4-trimethylpyrrole and (IV), respectively, (V) smoothly gives 4-benzoyl-3-phenyl-3':4':5:5'-tetramethylpyrromethene (hydrobromide, m.p. 230°) and 4-benzoyl-3-phenyl-3':5:5'-trimethyl-4'-ethylpyrromethene, m.p. 116° (hydrobromide, m.p. 213°). Attempts to condense (V) with Et 2:4-dimethylpyrrole-3-carboxylate in varied proportion gave mainly Et₂ 3:3':5:5'-tetramethylpyrromethene-4:4'-dicarboxylate (hydrobromide, m.p. 217°) (formed by autocondensation of the ester) with small amounts of (II), m.p. 212° (also +2MeOH). Similarly (VI) could not be condensed with 3-benzoyl-4-phenyl-2-methylpyrrole the "auto product" being 4:4'-dibenzoyl-3:3':5:5'-tetramethylpyrromethene (hydrobromide, m.p. 225°). Synthesis hampered by the heavy residues occurs only in a heated medium so that 2-free pyrroles which lead to autocondensation under

cold conditions more readily lose CHO under the experimental conditions than combine with the "difficult" pyrroles. (V) and 5-phenyl-3-methylpyrrole in abs. EtOH containing 48% HBr at 100° give 4-benzoyl-3:5'-diphenyl-3':5'-dimethylpyrromethene hydrobromide, m.p. 232°, whilst under like conditions 2:4-dimethylpyrrole-5-aldehyde (VII) yields 4-benzoyl-3-phenyl-2':4':5'-trimethylpyrromethene-5'-aldehyde hydrobromide, m.p. 210°, in which CHO is non-reactive. (IV) and (VII) in EtOH containing HBr give 3:3':5:5'-tetramethyl-4'-ethylpyrromethene, m.p. 80° (hydrobromide, m.p. 215°; picrate, m.p. 179°), Et 2:3-dimethylpyrrole-5-carboxylate is converted by BzCl and anhyd. AlCl₃ in boiling CS₂ into Et 4-benzoyl-2:3-dimethylpyrrole-5-carboxylate, m.p. 178°, hydrolysed to 4-benzoyl-2:3-dimethylpyrrole-5-carboxylic acid, m.p. 203° (decomp.), which passes at 220° into 4-benzoyl-2:3-dimethylpyrrole, m.p. 192°. The latter is transformed by anhyd. HCN-HCl in Et₂O into 4-benzoyl-2:3-dimethylpyrrole-5-aldehyde, m.p. 129°, which affords 3:3'-dibenzoyl-4:5:4':5'-tetramethylpyrromethene, decomp. 275° after softening at 210°. Protracted chlorination of Et 2:4-dimethyl-3-ethylpyrrole-5-carboxylate in CCl₄ leads to Et 2:4-di-(trichloromethyl)-3-ethylpyrrole-5-carboxylate, m.p. 65°, converted by conc. HNO₃ or conc. H₂SO₄ into the pentachloromonohydroxy-compound, C₁₁H₁₂O₃NCl₅, m.p. 111°. To examine the possibilities of the change CHR:CH·NH·CO₂Me → CH₂R·CHO in the pyrrole series, Me 5-carbethoxy-2:4-dimethylpyrrole-3-acrylate is converted into the corresponding hydrazide (VIII), m.p. 235° [hydrochloride, m.p. 215°; (CHPh), m.p. 241°, and Bz, m.p. 253°, derivatives; condensation products, C₁₈H₂₅O₅N₃, m.p. 178°, with C₂H₅Ac·CO₂Et and C₂H₅H₂O₅N₄, m.p. 304°, with (III)]. Et 2:4-dimethyl-3-β-dicarboxyhydrazidoethylpyrrole-5-carboxylate [dihydrochloride, m.p. 189°, and (CHPh)₂ derivative, m.p. 258° (decomp.)] and Et 2-methyl-4-ethyl-3-β-dicarboxyhydrazidoethylpyrrole-5-carboxylate, m.p. 233° [dihydrochloride, m.p. 181° (decomp.); (CHPh)₂ derivative, m.p. 263°], are described. Et 2:4-dimethyl-3-β-carboxy-β-carbethoxyethylpyrrole-5-carboxylate has m.p. 119°. (VIII) is converted by NaNO₂ and AcOH into the relatively stable azide, m.p. 141°, converted by SO₂Cl₂ in Et₂O into the compound, C₁₂H₁₃O₃N₄Cl, m.p. 136° (decomp.), which with boiling MeOH gives the substance, C₁₃H₁₆O₄N₄, m.p. 130° (decomp.). With boiling isoamyl alcohol, cholesterol, or CH₂Ph·OH in boiling xylene, the azide gives the respective urethanes, C₁₇H₂₆O₄N₂, m.p. 178°, C₃₉H₆₀O₄N₂, m.p. 217°, and C₁₉H₂₂O₄N₂, m.p. 200°, the last of which is transformed by SO₂Cl₂ in Et₂O into the compound, C₁₉H₂₀O₄N₂Cl₂, m.p. 158°, converted by 10% Na₂CO₃ and EtOH into the benzylurethane,



H. W.

New applications of magnesium in organic synthesis. II. Barbituric acid condensations. H. LUND (Kong. dansk. Vidensk. Selsk., mat.-fys. Medd., 1935, 13, No. 2, 9 pp.; Chem. Zentr., 1936, i, 2095—2096).—Mg may advantageously replace Na in such reactions, Mg(OMe)₂ in MeOH being superior to Mg(OEt)₂ in EtOH. In this manner barbituric

(86%), 5-isopropyl-, m.p. 214° (81%), 5-phenyl-, m.p. 258° (96%), 5:5-diallyl-, m.p. 170° (94%), 5-allyl-5-isopropyl-, m.p. 137° (81%), 5:5-diethyl-, m.p. 189° (81%), and 2-thio-5-isopropyl-, m.p. 178° (68%), -barbituric acids are obtained in the yields indicated. H. N. R.

Detection of therapeutically important barbituric acids. J. C. JESPERSEN and K. T. LARSEN (Arch. Pharm., 1937, 275, 28—35).—Barbituric acids are identified by their di-*p*-nitrobenzyl derivatives. The following are the corr. m.p. of the stated substituted barbituric acid, its xanthohydrate condensation product (prep. in hot AcOH), and the fully substituted *p*-nitrobenzyl derivative [prep. by $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{Cl}$ (prep. detailed) and Na_2CO_3 in aq. MeOH]: 5-Me*, 206.6°, —, 208°, -Et*, 191.5°, —, 213.5°, -Pr, 216.7°, 207.5°, 189°, 5:5-Et₂, 188.5°, 246.5°, 193.5°, -Pr₂, 146.5°, 269°, 182.3°, -ethyl-*n*-butyl, 122.5°, 250°, 148.5°, -ethylisomethyl, 141°, 251°, 145.5°, -ethylallyl, 159.4°, 242°, 196.3°, -isopropylallyl, 139.5°, 226.5°, 192°, -*n*-butylallyl, 126.1°, 240°, 127.5°, -isobutylallyl*, 135.9°, —, —, diallyl, 171.5°, 242.5°, 192.5°, 5-phenyl-5-methyl, 223.7°, 282°, 197°, 5-phenyl-5-ethyl, 174.9°, 219°, 183.5°, 5-phenyl-5-allyl, 154.9°, 222.5°, 152°, isopropylbromopropenyl, —, —, 200.5°, 5-cyclohexenyl-5-ethyl, 176.4°, 257°, 196°, 5-phenyl-1-methyl-5-ethyl, 173.2°, —, 114.5°, 5-cyclohexenyl-1:5-dimethyl, 143.9°, —, 114.5°. The solubilities of the acids, except those marked *, in H₂O at 20° and 37° are recorded. In most cases the acids are readily analysed by treatment in CHCl₃ with aq. KBr-KBrO₃ and determination of the excess of KBrO₃; the addition is complete in 15 min. R. S. C.

2-Alkylbenzimidazoles as derivatives for identification of aliphatic acids. W. O. POOL, H. J. HARWOOD, and A. W. RALSTON (J. Amer. Chem. Soc., 1937, 59, 178—179).—2-Alkylbenzimidazoles (I) are prepared from $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and AlkCO_2H (II) (Alk = Me—*n*-heptadecyl) by a slight modification of Seka and Müller's method (A., 1931, 600). The higher (I) have similar m.p. and are not very useful for identifying (II). The following appear to be new: 2-*n*-octyl-, m.p. 139.5—140.5° (all m.p. are corr.), -*n*-decyl-, m.p. 114—114.5°, -*n*-dodecyl-, m.p. 109—109.5°, -*n*-tridecyl-, m.p. 105—105.5°, -*n*-tetradecyl-, m.p. 98.5—99.5°, and -*n*-hexadecyl-, m.p. 93.5—94.5°, -benzimidazoles. H. B.

Preparation of *p*-phenanthroline and 3:3'-dipyridyl. M. I. KABATSHNIK and V. V. REZON (J. Appl. Chem. Russ., 1936, 9, 2026—2029).— $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-NO}_2$, glycerol, and H₂SO₄ (1 hr. at 130°, 1.25 hr. at 130—150°, and 1.25 hr. at 150—160°) yield *p*-phenanthroline, from which 3:3'-dipyridyl is prepared by known methods. R. T.

Transformation products of some hydrazides of organic acids. I. (SIGNA.) M. FRERI (Atti V Congr. Naz. Chim., 1936, 1, 361—365).—Et crotonate with N₂H₄.H₂O yields crotonhydrazide, which could not be converted into the azide, but gave 1-nitroso-5-methylpyrazolidone, m.p. 173°. Et β-chloroisocrotonate does not give the hydrazide, but with N₂H₄.H₂O forms methylpyrazolone, also obtained from Me isocrotonate. Me₂ itaconate (new prep. from Na salt

and Me₂SO₄) yields itacondihydrazide, m.p. 150° (decomp.), converted into the -diazide, m.p. 50°. Me₂ mesaconate yields mesacondihydrazide, m.p. 215° (decomp.), converted into the -diazide, m.p. 113° (decomp.). Citracondihydrazide, m.p. 212°, with HNO₂ gives the diazide, m.p. 114°, further converted into 3:6-diketo-4-methyl-1:2:3:6-tetrahydropyridazine, m.p. 277°, also obtained directly from citraconic anhydride (1 mol.) and N₂H₄.H₂O (1 mol.). With excess of HNO₂, the dihydrazide yields a compound, C₄H₅O₂N₃, m.p. 231° (coloured Na, K, and Ag salts; Bz derivative, m.p. 177°; $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CO}$ derivative, m.p. 188°), and a compound, m.p. 245°. E. W. W.

Chemiluminescent organic compounds. I. Isomeric simple and complex hydrazides of phthalic acid and mode of formation of phthalazine and isoindole rings. H. D. K. DREW and H. H. HATT. II. Effect of substituents on the closure of phthalylhydrazides to 5- and 6-membered rings. H. D. K. DREW and F. H. PEARMAN. III. *N*-Methylated phthalaz-1:4-diones. H. D. K. DREW, H. H. HATT, and F. A. HOBART (J.C.S., 1937, 16—26, 26—33, 33—37).—I. Phthalaz-1:4-dione (I) is prepared by condensation of $o\text{-C}_6\text{H}_4(\text{CO}_2)_2\text{O}$ (II) and N₂H₄ in AcOH and is $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ (cf. Curtius et al., A., 1895, i, 354). With excess of (II), *N*-phthalimidophthalimide (III), m.p. 311—313°, is obtained, hydrolysed with N₂H₄ to (I) and with NaOH to *s*-dibenzoylhydrazine-2:2'-dicarboxylic acid (IV). Short-period reaction of (II) with N₂H₄ in AcOH or EtOH leads to variable amounts of *N*-aminophthalimide (V), which at its m.p. (200—205°) is changed to (I) (cf. Rothenburg, A., 1894, i, 285), and condenses with aldehydes to give *N*-acetamidophthalimide, m.p. 228—230°, and *N*-isopropylidene-, m.p. 97—100°, -benzylidene-, m.p. 166—167°, -*p*-anisylidene-, m.p. 189—191°, -cinnamylidene-, m.p. 199—200°, and -piperonylidene-aminophthalimide, m.p. 186.5—170°. $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NH}$ and N₂H₄ in EtOH give *o*-carbamylylbenzhydrazide, m.p. 300—320°, converted into (I) and (V) in boiling EtOH. (I) with aldehydes yields the same products as from (V) but with CHPh:CH:CHO affords 3-phenyl-1:2-phthalopyrazolone, m.p. 224—228°, which with NaOEt-EtOH forms 5-phenylpyrazoline; these reactions show conversion from the 6- into the 5-membered ring. (V) and (II) in AcOH give (III) (*N*-3', m.p. 249—250°, and -4'-nitrophthalimidophthalimide, m.p. 250°). *o*-Carbomethoxybenzoyl chloride (VI) and N₂H₄ in C₅H₅N yield *Me s*-dibenzoylhydrazine-2:2'-dicarboxylate, m.p. 180—200°, cyclised to (III) and hydrolysed to (IV), m.p. 260—320° (hydrazine and Ag salts), which is also partly cyclised to (III). *Me s*-dibenzoyldimethylhydrazine-2:2'-dicarboxylate, m.p. 171—172°, is unchanged by fusion. The formation of (V) appears not to be utilised in the production of (III).

Excess of (II) and N₂H₄ in AcOH, reacting for 0.5 min., give *N*-phthalimidophthalamic acid, decomp. 160—190° (Ag salt), cyclised to (III) (70%), (I), and (II), and also prepared from (V) and (II). *Me N*-phthalimidophthalamate, m.p. 166—168°, is obtained from (V) and (VI), cyclised to (III). The probable

course of the reactions is discussed. (VI) and (I) condense to 2-*o*-carbomethoxybenzoylphthalaz-1:4-dione, decomp. 165–170°, cyclised to (III). (I) and *s*-phthalyl chloride in PhNO_2 afford 2:3-phthalophthalaz-1:4-dione, m.p. 350–360° (slight decomp.), converted by N_2H_4 into (I). (I) with Ac_2O yields 4-acetoxy-2-acetylphthalaz-1-one, m.p. 139–140°, and with AcCl in $\text{C}_5\text{H}_5\text{N}$ gives an *Ac* derivative, m.p. 175–176°; a second *Ac* derivative is obtained by partial hydrolysis of the Ac_2 compound (cf. Rowe and Peters, A., 1933, 1308). These results are in favour of the structure assigned to (I) and not the enol forms.

II. 5-Nitrophthalaz-1:4-dione forms two *Ac* derivatives, m.p. 221° (cf. Mihailescu *et al.*, A., 1930, 1434) and m.p. 205°. 3-Nitro-2-carboxybenzhydrazide, m.p. 298–300°, is obtained from its 2-hydrazine salt. 5-Aminophthalaz-1:4-dione (VII) forms 5-acetamido-, m.p. 325–326° (decomp.), and 5-benzamido-phthalaz-1:4-dione, m.p. 319° (decomp.), and a Bz_2 derivative, m.p. 263°. 3-Aminophthalimide and N_2H_4 (1 mol.) give *N*:3-diaminophthalimide, m.p. 252° (3-acetamido-*N*-anilinophthalimide, m.p. 179°); with 2 mols. of N_2H_4 (VII) is obtained. 4-Aminophthalimide and N_2H_4 form only 6-aminophthalaz-1:4-dione, m.p. 339° (decomp.) [*Ac* derivative, m.p. 341° (decomp.)]. 3-Nitro-*N*-anilinophthalimide, m.p. 188°, and *s*-bis-(6-nitro-2-carboxybenzoyl)hydrazine, m.p. about 318° (decomp.), are described. 3-Chlorophthalimide with 1 mol. of N_2H_4 forms 3-chloro-*N*-aminophthalimide, m.p. 194–195°, but with 2 mols., 5-chlorophthalaz-1:4-dione, m.p. 338° (decomp.) (azo-compound), is obtained. 3:6-Dichlorophthalimide with N_2H_4 (1 mol.) forms 3:6-dichloro-*N*-aminophthalimide, m.p. 210° (benzylidene derivative, m.p. 224°), resolidifying to yield 3:6:3':6'-tetrachloro-*N*-phthalimidophthalimide, m.p. above 350°; with 2 mols. of N_2H_4 , it gives the hydrazine salt of 3:6-dichloro-2-carboxybenzhydrazide, dehydrated to 3:6-dichlorophthalodihydrazide. 3:6-Dichlorophthalic anhydride with excess of N_2H_4 affords 5:8-dichlorophthalaz-1:4-dione, m.p. above 350°, and with N_2H_4 in AcOH gives *s*-bis-(3:6-dichloro-2-carboxybenzoyl)hydrazine, m.p. above 350°, converted with N_2H_4 into hydrazine 3:6-dichlorophthalate, m.p. 206°. 4:5-Dichlorophthalic anhydride with N_2H_4 yields only 6:7-dichlorophthalaz-1:4-dione, m.p. above 350°. Tetrachlorophthalic acid or anhydride with N_2H_4 gives only 3:4:5:6-tetrachloro-*N*-aminophthalimide, m.p. 288° (decomp.) (benzylidene derivative, m.p. 232°), which with the anhydride forms octachloro-*N*-phthalimidophthalimide, m.p. above 350°. 3-Hydroxyphthalimide, m.p. 255–256°, with N_2H_4 , gives only 5-hydroxyphthalaz-1:4-dione, m.p. 330° (decomp.) (*Na* salt). The mechanism and conditions for the reactions are discussed.

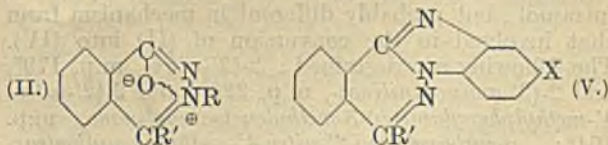
III. (II) (see above) with $(\text{NHMe})_2\cdot 2\text{HCl}$ gives 2:3-dimethylphthalaz-1:4-dione, m.p. 175–176° (+2 H_2O), and with $\text{NMe}_2\cdot\text{NH}_2$ forms *N*-dimethylaminophthalimide, m.p. 125–126°. 3-Nitrophthalic anhydride (VIII) and $\text{NMe}_2\cdot\text{NHMe}$ yield a mixture of α -, m.p. 292° (decomp.) (*Ac* derivative, m.p. 204–205°), and β -5-nitro-*N*-methylphthalaz-1:4-dione, m.p. 272° (decomp.) (*Ac* derivative, m.p. 158°), reduced to the corresponding α -, m.p. 308°, and β - NH_2 -compounds, m.p. 299° (decomp.). (VIII) and $(\text{NHMe})_2$ form 5-nitro-2:3-dimethylphthalaz-1:4-dione, m.p.

194–195°, reduced to the 5- NH_2 -derivative, m.p. 192° [*Ac* derivative, m.p. 221–222°; azo-compound, m.p. 312–316° (decomp.)]; with $\text{NMe}_2\cdot\text{NH}_2$, 3-nitro-*N*-dimethylaminophthalimide, m.p. 141–142°, is obtained. 4-Nitrophthalic anhydride with $\text{NMe}_2\cdot\text{NHMe}$ gives a mixture of α -, m.p. 307° (decomp.) (*Ac* derivative, m.p. 210°), and β -6-nitro-*N*-methylphthalaz-1:4-dione, m.p. 293° (decomp.) [*Ac* derivative, m.p. 195° (decomp.)], reduced to the α -, m.p. 320° (decomp.), and β -6- NH_2 -compounds, m.p. 360° (decomp.). 6-Nitro-, m.p. 198–199°, reduced to 6-amino-2:3-dimethylphthalaz-1:4-dione, m.p. 262–263° [+2 H_2O ; *Ac* derivative (+ H_2O), m.p. 269–270°; azo-compound, m.p. 270–272°], and 4-nitro-*N*-dimethylaminophthalimide, m.p. 152–153°, are similarly prepared. The conclusion is reached that the substitution of immobile groups for two of the enolisable H of phthalaz-1:4-diones removes the luminescence, and that such substitution of one of them greatly diminishes, if it does not entirely remove, that property. F. R. S.

Chemiluminescence with two organic reactions. G. VÉSZI (Tech. Kurir, 1937, 8, No. 2, 1–3). —A lecture. On oxidation of 10:10'-dimethyl-5:5'-diaeridinium dinitrate and of 3-aminophthalhydrazide with H_2O_2 intense chemiluminescence is observed.

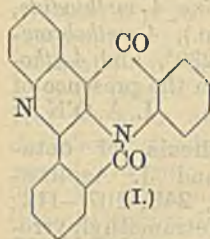
E. P.

Reaction of certain diazosulphonates derived from β -naphthol-1-sulphonic acid. XVII. Conversion of nitro-3-aryl- and nitro-3-aryl-4-methyl-phthalaz-1-ones into corresponding phthalaz-4-ones by migration of the nitroaryl group, and related reactions. F. M. ROWE, D. A. W. ADAMS, A. T. PETERS, and (in part) E. A. GILLAM (J.C.S., 1937, 90–109). —The action of HCl aq. on $\text{o-C}_6\text{H}_4\text{C}(\text{OH})=\text{CH}_2(\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{NR}$ (I) ($\text{R} = \text{NO}_2\cdot\text{C}_6\text{H}_4$ or $\text{NH}_2\cdot\text{C}_6\text{H}_4$) and the conversion of (II) ($\text{R} = \text{nitroaryl}$; $\text{R}' = \text{H}$ or Me) into the corresponding



compounds $\text{C}_6\text{H}_4\text{C}(\text{CO}\cdot\text{NR})=\text{CH}_2\text{NR}$ (IV) have been fully investigated and a property peculiar to 2'- NO_2 -compounds has now been observed. Thus, 2'-amino-3-arylphthalaz-4-ones, and the corresponding 1-Me compounds, convertible into 2':4-anhydro-derivatives (V) ($\text{R}' = \text{H}$ or Me ; $\text{X} = \text{H}$, Me , or Cl) by aq. HCl at 180°, are obtained satisfactorily only from the corresponding compounds $\text{o-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CR}'\cdot\text{N}\cdot\text{NHR}$ (III), as reduction of (IV) ($\text{R} = 2'$ -nitroaryl; $\text{R}' = \text{H}$ or Me) with Na_2S ($\text{EtOH-H}_2\text{O}$) probably gives mainly hydroxylamine derivatives. Compounds (II) ($\text{R} = \text{nitroaryl}$; $\text{R}' = \text{H}$ or Me) are usually best converted into the corresponding (IV) by heating with N-HCl at 170–190°. The reaction is approx. unimol., whilst the rate is influenced markedly by the concn. of the acid used, the nature and position of substituents in R , and, in certain cases, by the temp. A mechanism, involving migration of R , but intramol. and not involving free

oline, m.p. 223°, whence 2-chloro-6-methyl-3:4-N-anilinoindoloquinoline, m.p. 214° (hydrochloride), and 2-anilino-6-methyl-3:4-N-anilinoindoloquinoline, m.p. 256°. (V) is oxidised by KMnO_4 in presence of $\text{Mn}(\text{OAc})_2$ into 2-amino-5-methylbenzoic acid and (?) 2-N-oxalylamino-5-methylbenzoic acid. 1:4-Diketo-2-phenyltetrahydroisiquinoline, m.p. 149°, and 1:3-diketo-2-anilinohydrindene, m.p. 215°, and the corresponding acid, $\text{C}_{15}\text{H}_{13}\text{O}_5\text{N}$, m.p. 137°, do not condense with isatin. The similarity of the reactions of (I), (II), (III), and (IV) supports the annexed structure for (I).



H. W.

Aromatic nitro-derivatives. IX. 1-Bromo-3:4-dinitrobenzene. A. MANGINI (Gazzetta, 1936, 66, 675—684; cf. A., 1936, 1244).—In 1:3:4- $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)_2$ (I) the 3- NO_2 is reactive. With NaOEt or KOH-EtOH , (I) forms 5-bromo-2-nitrophenetole, m.p. 79.5—80.5°, reduced with difficulty (Sn-HCl) to the hydrochloride, m.p. 199—200° (decomp.) of 5-bromo-2-aminophenetole [picrate, m.p. 172—173° (decomp.)]; the hydrochloride with $\text{NaOAc-Ac}_2\text{O}$ gives 5-bromo-2-acetamidophenetole, m.p. 118—119°. With piperidine followed by HCl , (I) gives 5-bromo-2-nitrophenylpiperidine hydrochloride, m.p. 152—153.5° [to a cloudy melt, clearing at 156—157° (decomp.)]; 2:5:1- $\text{C}_6\text{H}_3\text{Br}_2\text{NO}_2$ yields 4-bromo-2-nitrophenylpiperidine hydrochloride, m.p. 143—144° [to a cloudy melt, clearing at 153—154° (decomp.)]. With $\text{NH}_2\text{-NH-CS-NH}_2$, (I) gives, even in presence of MgCO_3 , bis-(5-bromo-2-nitrophenyl) disulphide, m.p. 184—185°, also obtained using $\text{CS}(\text{NH}_2)_2$ or OEt-CS-SK . 5-Bromo-2-nitrophenylhydrazine hydrochloride and NH_4SCN are needed to form the expected 5-bromo-2-nitrophenylthiosemicarbazide, m.p. 207—208°. The above hydrazine in boiling KOH-EtOH , or heated above its m.p., yields 5-bromo-1-hydroxybenzotriazole, m.p. 201.5—202.5° (exploding); the isomeric 6-bromo-1-hydroxybenzotriazole, m.p. 188—190°, is obtained from $\text{N}_2\text{H}_4\text{-H}_2\text{O}$ and 2:5:1- $\text{C}_6\text{H}_3\text{Br}_2\text{NO}_2$. The last with NHPH-NH-CS-NH_2 gives bis-(4-bromo-2-nitrophenyl) sulphide.

E. W. W.

Catalytic reductions in the γ -triazine group. I. Conversion of dihydroxymethyltriazine into the "trigenic acid" of Liebig and Wöhler. A. OSTROGOVICH and G. OSTROGOVICH (Atti V Congr. Naz. Chim., 1936, 1, 427—431).—Dihydromethyltriazine is hydrogenated (Pt) to 2:4-diketo-6-methyltriazidine, m.p. 272—273° (decomp.) (acetate; hemihydrochloride; hemiaurichloride; hemipicrate; basic Hg_2 salt; Ac_2 derivative, m.p. 171—172°), identical with "trigenic acid." The reduction is also effected by Al-Hg and, less satisfactorily, by Na-Hg or Sn-HCl .

E. W. W.

γ -Triazines. XXXIII. New compounds obtained from dihydroxytriazinylformaldoxime. A. OSTROGOVICH and V. CRASU. XXXIV. Dihydroxytriazinyl phenyl ketoxime and its salts. XXXV. Beckmann transformation of dihydroxytriazinyl phenyl ketoxime. A. OSTROGOVICH and I. TANISLAU (Gazzetta, 1936, 66, 653—662,

662—671, 672—684).—XXXIII. Dihydroxytriazinylformaldoxime (I) (cf. A., 1935, 225) with Ac_2O gives only an acetate; in presence of $\text{C}_6\text{H}_5\text{N}$ the product is the $(\text{C}_6\text{H}_5\text{N})_2$ salt, converted over H_2SO_4 into the $\text{C}_6\text{H}_5\text{N}$ salt, m.p. 177—178° (decomp.), of the Ac derivative, m.p. 203—204° (decomp.). The $(\text{C}_6\text{H}_5\text{N})_2$ and $\text{C}_6\text{H}_5\text{N}$ salts of the Bz derivative, m.p. 187—188° (decomp.), are similarly prepared. When the above are heated in $\text{C}_6\text{H}_5\text{N}$, they give the $(\text{C}_6\text{H}_5\text{N})_2$ salt, which can be converted into the $\text{C}_6\text{H}_5\text{N}$ salt of dihydroxytriazinylformonitrile (Na , K , Ag , and Ba salt). (I) heated in dil. AcOH with NHPH-NH_2 forms the acetate, decomp. 115—120°, of dihydroxytriazinylformaldehyde phenylhydrazone (dihydrochloride; sulphate); the corresponding phenylmethylhydrazone (monohydrochloride; sulphate) is also prepared. (I) is reduced ($\text{SnCl}_2\text{-HCl}$) to the hydrochloride of dihydroxytriazinylmethylamine (stannichloride; sulphate; picrate; Ac derivative), which does not give a Schiff's base. In dil. HCl with $\text{CO}_2\text{-H}_2\text{S}$ (I) yields dihydroxytriazinylthioformamide ($+\text{H}_2\text{O}$, lost at 110—115°) (NH_4 salt, also obtained from the nitrile and NH_4SH). The Na salt of the last, or of the nitrile, with NH_2OH gives the Na salt, m.p. $>310^\circ$, of dihydroxytriazinylformamidoxime (Ag salt). The last, or the thioamide, with NHPH-NH_2 in EtOH , yields dihydroxytriazinylformphenylhydrazidine, $(\text{C}_6\text{H}_5\text{O}_2\text{N}_3)\cdot\text{C}(\text{NH}_2)\cdot\text{N-NHPH}$. With $\text{Br-H}_2\text{O}$, (I) gives dihydroxytriazinylbromoformaldoxime, $(\text{C}_6\text{H}_5\text{O}_2\text{N}_3)\cdot\text{CBr}\cdot\text{N}\cdot\text{OH}$ ($+\text{2H}_2\text{O}$).

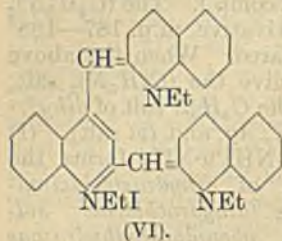
XXXIV. Dihydroxybenzyltriazine (A., 1935, 225) with $\text{C}_6\text{H}_{11}\text{O}\cdot\text{NO}$ in AcOH-HCl yields dihydroxytriazinyl Ph ketoxime [$+\text{3H}_2\text{O}$, m.p. 235—236°; $+\text{2H}_2\text{O}$, m.p. 241—242°; $+\text{H}_2\text{O}$, m.p. 255—256° (all decomp.)] [monohydrochloride, m.p. 226—227° (decomp.); no sulphate]. This gives Na ($+\text{3H}_2\text{O}$), m.p. 269—271° (decomp.); Na ($+\text{H}_2\text{O}$); Na_2 ($+\text{1.5EtOH}$), m.p. 264—265° (decomp.); Na_2 ; Ag ($+\text{H}_2\text{O}$), m.p. 300—302° (decomp.); Ag ; Ba ($+\text{3H}_2\text{O}$), m.p. 252—253° (decomp.); Ba ; Fe^{II} ($+\text{4H}_2\text{O}$), greenish-grey, m.p. 228—230° (decomp.); Fe^{II} , yellow (formed from the last at 150°); Cu ($+\text{2H}_2\text{O}$); and Cu , m.p. 321—322° (decomp.), salts. The co-ordinated structure of the Fe^{II} and Cu salts is discussed.

XXXV. Since dihydroxytriazinyl Ph ketoxime is converted by $\text{PCl}_5\text{-AcCl}$ into N-benzoylammelide (benzamido-dihydroxytriazine), m.p. 263—264° (hydrolysed by $\text{NH}_3\text{-EtOH}$ at 110° toammelide and NH_2Bz), it is presumed to have the *anti* structure (OH anti to triazine ring).

E. W. W.

Cyanine dye series. VII. Dyes containing three heterocyclic nuclei. L. G. S. BROOKER and L. A. SMITH (J. Amer. Chem. Soc., 1937, 59, 67—74).—2-Iodo-4-methylquinoline ethiodide (I), m.p. 218—219° (decomp.) (obtained by prolonged action of EtI on 2-chloro-4-methylquinoline in the dark), and 2-methylquinoline ethiodide (II) in EtOH-NEt_3 give (after treatment with KClO_4) 4-methyl-1:1'-diethyl-2:2'-cyanine perchlorate, m.p. 279—280° (decomp.); the corresponding iodide is also obtained together with 2'-methyl-1:1'-diethyl-2:4'-cyanine iodide (III) [modified prep. from (II) and EtOH-KOH] from equimol. quantities of 2-iodo- (IV) and 2:4-dimethyl- (V), m.p. 231—233°, -quinoline ethiodide in EtOH-

NEt₃. (IV) (4 mols.) and (V) (1 mol.) similarly afford 2% of 2:4-di-(1-ethyl-1:2-dihydro-2-quinolylidenemethyl)quinoline ethiodide (VI), m.p. 291—292° (decomp.), also obtained in 4.5% yield from (III) and (IV) (excess) and in 6.5% yield from (II) (excess) and 2:4-di-iodoquinoline ethiodide (VII), m.p. 235—236° (decomp.) [from 2:4-dichloroquinoline (modified prep.) and EtI at 100°/3 weeks]. The absorption curve of (VI) shows max. at 4550 (weak), 4800, and 6150 Å.; between the two principal bands there is a region



of almost complete transmission with min. absorption at about 5150 Å. The unusual absorption of (VI) is ascribed to the presence in the mol. of linkings characteristic of three distinct cyanine types. 2:4-Di-(1-methyl-1:2-dihydro-2-quinolylidenemethyl)quinoline methiodide (VIII), m.p. >310° (decomp.) (shrinks from about 300°), and 2:4-di-(1-ethyl-1:2-dihydro-2-quinolylidenemethyl)quinoline methiodide (IX), m.p. 302—303° (decomp.), -1:2-dihydro-2-quinolylidenemethyl)quinoline methiodides are similarly prepared from 2:4-di-iodoquinoline methiodide, m.p. 236—237° (decomp.) (with 2-methylquinoline methiodide), and 2:4-dimethylquinoline methiodide, m.p. 271—272° [with (IV)], respectively. (VIII) has a stronger sensitising action than either (VI) or (IX). 1-Methylbenzthiazole etho-*p*-toluenesulphonate (X) (4 mols.) and (VII) (1 mol.) in EtOH-NEt₃ give a little 2:4-di-(2-ethyl-1:2-dihydro-1-benzthiazolidenemethyl)quinoline ethiodide, m.p. 274—276° (decomp.), which is a better sensitiser than (VI). 2:4-Di-(2-methyl-1:2-dihydro-1-benzthiazolidenemethyl)quinoline methiodide, m.p. 301—302° (decomp.), is similarly prepared. A dye containing three quinoline nuclei could not be obtained from 4-methylquinoline ethiodide and (VII); 4-iodo-1:1'-diethyl-2:4'-cyanine iodide, m.p. >300°, is probably formed. (I) and (X) afford 4'-methyl-2:1'-diethylthia-2'-cyanine iodide, m.p. 276—277.5° (decomp.), whilst (I) and 1-methyl-β-naphthiazole etho-*p*-toluenesulphonate give 4'-methyl-2:1'-diethyl-3:4-benzothia-2'-cyanine iodide, m.p. 272—274° (decomp.). 2'-Iodo-4-methyl-1:1'-diethyl-2:4'-cyanine iodide, m.p. 231—232° (decomp.), is obtained from (I) and EtOH-NEt₃.

H. B.

5-Anilinetetrazole. R. STOLLÉ and K. HEINTZ (J. pr. Chem., 1937, [ii], 147, 286).—The main product of the action of NaN₃ on NH₂·CO·NHPh and whitelead in EtOH is 5-amino-1-phenyltetrazole (A., 1922, i, 689); 5-anilinetetrazole, m.p. 206°, is produced in minor amount.

H. W.

Optical sensitisers. II. C. GASTALDI and E. PRINCIVALE (Annali Chim. Appl., 1936, 26, 450—455).—A series of sensitisers, 3:3'-diketo-1:1':4:4':5:5'-hexamethyl-2:2'-monostreptovinyl-enepyrzinecyanine 1-iodide, m.p. 280°, 1-chloride, m.p. 277°, 1-bromide, m.p. 275°, and the corresponding -1:1':5:5'-tetramethyl-1-iodide, m.p. 262°, 1-chloride, m.p. 292°, and 1-bromide, m.p. 280°, and 5:5'-dimethyl-1:1'-diethylpyrzanecyanine 1-iodide, m.p. 272°, and 1-bromide, m.p. 265°, has been prepared by condensing 6-keto-1:2:5-trimethyl-1:6-dihydropyrazine 4-methiodide (A., 1928, 1027), 4-

methochloride, and 4-methobromide, m.p. 258°, 6-keto-2:5-dimethyl-1:6-dihydropyrazine 4-methiodide, m.p. 248°, 4-methochloride (decomp.), 4-methobromide, m.p. 257°, 4-ethiodide, m.p. 230°, and 4-ethobromide, m.p. 250°, with CH(OEt)₂ in the presence of Ac₂O.

L. A. O'N.

Bile pigments. XVI. Synthesis of octamethylbilirubin. H. FISCHER and J. ASCHENBRENNER (Z. physiol. Chem., 1937, 245, 107—112; cf. A., 1936, 346).—3:3':4:4'-Tetramethylpyrromethene-5:5'-dicarboxylic acid in AcOH gives with Br in AcOH a mixture (I) of 5:5'-dibromo-3:3':4:4'-tetramethylpyrromethene hydrobromide (II) and 5-bromo-3:3':4:4'-tetramethylpyrromethene-5'-carboxylic acid, which is converted into (II) by further treatment with Br in AcOH. (I) with KOH in MeOH gives 5-methoxy-3:3':4:4'-tetramethylpyrromethene-5'-carboxylic acid (III), m.p. 216° [Me ester, m.p. 152—153°; K salt, m.p. 292° (decomp.)], and 5'-bromo-5-methoxy-3:3':4:4'-tetramethylpyrromethene, m.p. 144°. (III) with KOH in PrOH at 190—200° for 2 hr. gives 5-hydroxy-3:3':4:4'-tetramethylpyrromethene, m.p. 290°, which, with CH₂O and conc. HCl gives octamethylbilirubin [corresponding cryst. ferrobin, m.p. 282° (decomp.)]. Similarly (II) gives dimethoxyoctamethylbilirubin, m.p. 245° (decomp.). (I) in MeOH with excess of NH₂Ph gives 5-anilino-3:3':4:4'-tetramethylpyrromethene-5'-carboxylic acid, m.p. 246° (Me ester, m.p. 199°), and similarly (II) gives 5:5'-dianilino-3:3':4:4'-tetramethylpyrromethene, m.p. 245° (hydrobromide, m.p. 285°).

W. McC.

Reversible oxidation and reduction of chlorophyll. E. RABINOWITCH and J. WEISS (Nature, 1936, 138, 1098—1099).—Et chlorophyllide in MeOH solution is reversibly oxidised by FeCl₃ with a change in colour to greenish-yellow and a diminution in fluorescence. Prompt addition of FeCl₂ restores the original colour and fluorescence. The first product of oxidation is unstable, and reacts further either with the FeCl₃ or possibly with dissolved O₂. Oxidation is favoured by illumination with red light.

L. S. T.

Chlorophyll. LXXI. Quantitative dehydrogenation of chlorin copper salts with oxygen. H. FISCHER and K. HERRLE (Annalen, 1937, 527, 138—140).—The absorption of O by chlorin-Cu complex salts in AcOH containing Cu(OAc)₂ at 40° occurs with quant. formation of porphyrin Cu salts only in the cases of mesopyrro- and mesorhodo-chlorin. Other chlorins are dehydrogenated with difficulty on account of their constitution or are in part completely decomposed particularly if CH:CH is present.

H. W.

Porphyrins. XL. Synthesis of 1:3:5:7-tetramethylporphyrin-2:4:6:8-tetrasuccinic acid. H. FISCHER and H. ZISCHLER (Z. physiol. Chem., 1937, 245, 123—138; cf. A., 1935, 363; this vol., 36).—5-Carboxy-2:4-dimethylpyrrol-3-succinic acid (I) in AcOH gives with 3 mols. of Br in AcOH 5-bromo-5'-bromomethyl-4:3'-dimethylpyrromethene-3:4'-disuccinic acid hydrobromide, m.p. >280°. When 2 mols. of Br are used material is obtained which, when fused with methylsuccinic acid and esterified with

HCl in MeOH, gives the Me_8 ester (II), m.p. 255° (Cu salt, m.p. 260°, Fe salt), of 1 : 3 : 5 : 7-tetramethylporphyrin-2 : 4 : 6 : 8-tetrasuccinic acid. (II) is spectroscopically but not otherwise identical with the Me_8 ester of natural uroporphyrin. (II) heated with dil. HCl for 3 hr. at 180° gives coproporphyrin I. (I) decarboxylated in dil. HCl at 40° gives 2 : 4-dimethylpyrrol-3-succinic acid (III), m.p. 180° (decomp.). The Et_2 (IV) and Me_2 esters of 5-carbomethoxy-2 : 4-dimethylpyrrol-3-succinic acid (Na_2 salt) have m.p. 79° and 103°, respectively. (I) with CH_2N_2 gives the Me_2 ester, m.p. 121—122°, of 5-carbomethoxy-2 : 4-dimethylpyrrol-3-succinic acid. (IV) with Br in AcOH gives the Et_2 ester (V), m.p. 103°, of 5-carbomethoxy-4-methyl-2-bromomethylpyrrol-3-succinic acid and with SO_2Cl_2 the Et_2 ester (VI), m.p. 105°, of the corresponding 2- CH_2Cl derivative. (V) and (VI) give with MeOH the corresponding 2-OH- CH_2 derivative, m.p. 57—58°. (IV) with $N_2H_4 + H_2O$ gives 5-carbomethoxy-2 : 4-dimethylpyrrol-3-succinic acid dihydrazide, m.p. 200° [hydrochloride (VII), m.p. 213°]. (VII) with dil. HCl + $NaNO_2$ gives the corresponding diazide, which, when boiled with EtOH, yields the corresponding diethylurethane, m.p. 180—220° (decomp.). Pyrrole-2-aldehyde (VIII) in presence of HBr with the Na_3 salt of 5-carboxy-2 : 4-dimethylpyrrol-3- β -methylmalonic acid gives the hydrobromide, m.p. 180—205° (decomp.), of 3' : 5'-dimethylpyrromethene-4'- β -methylmalonic acid [Et_2 ester (IX), m.p. 161°]. (IX) with Br in AcOH gives the corresponding 3 : 4 : 5- Br_3 -compound, which when fused with succinic acid yields Me_2 1 : 5-dimethylporphyrin-2 : 6-dipropionate. (III) with (VIII) in presence of HBr gives the hydrobromide, decomp. 180° (Me_2 ester, m.p. 150°), of 3' : 5'-dimethylpyrromethene-4'-succinic acid. W. McC.

Spectra of adsorbed porphyrin.—See A., I, 61.

Spectra of heliocorubin and oxyheliocorubin.—See A., III, 83.

Pyrrole-blacks. P. PRATESI (Atti V Congr. Naz. Chim., 1936, 1, 463—466).—A review. Pyrrole-blacks contain linked pyrrole nuclei oxidised in the 2-position. E. W. W.

Derivatives of quinoline. I. Nupercaine analogues. I. M. E. SMITH and C. B. POLLARD (J. Amer. Chem. Soc., 1937, 59, 131—132).—N-Phenyl-N'-2-chlorocinchonylpiperazine (I), m.p. 189.2—190.2°, and N-2-chlorocinchonylmorpholine (II), m.p. 173.6—174.4°, are prepared from 2-chlorocinchonyl chloride (in C_6H_6) and the appropriate base (in aq. Na_2CO_3). (I) and AlkOH-NaOAlk in C_6H_6 give N-phenyl-N'-2-methoxy-, m.p. 149.5—150.2°, -ethoxy-, m.p. 154—154.5°, -n-propoxy-, m.p. 102.8—103.3°, -isopropoxy-, m.p. 116.2—117.2°, -n-butoxy-, m.p. 77.2—78.2°, -allyloxy-, m.p. 129.5—130.5°, and - β -methoxyethoxy-, m.p. 91.6—92.3°, -cinchonylpiperazines; (II) similarly affords N-2-methoxy-, m.p. 134—134.9°, and -ethoxy- (III), m.p. 69—69.8°, -cinchonylmorpholines. NN'-Di-2-chlorocinchonyl-, m.p. >300°, and N-phenyl-N'-(2- β -N-phenylpiperazinoethoxycinchonyl)-, m.p. 134.7—135.2°, -piperazines are described. All m.p. are corr. (III) has pronounced anaesthetic activity. H. B.

Condensation products of s-diphenylcarbazide and sugars. A. SANNA (Atti V Congr. Naz. Chim., 1936, 1, 528—530).—Either arabinose or xylose with s-diphenylcarbazide in boiling AcOH-NaOAc (H_2) yields 3-hydroxy-1-phenyl-5- α -furyl-1 : 2 : 4-triazole, m.p. 160° (decomp.) (cf. A., 1915, i, 596).

E. W. W.

Formation and reactions of substituted thiazolidones. IV. F. A. EBERLY and F. B. DAINS (J. Amer. Chem. Soc., 1936, 58, 2544—2547; cf. A., 1936, 347).—Allylthiocarbamide and $CH_2Cl \cdot CO_2H$ in H_2O or EtOH give 2-imino-3-allyl-4-thiazolidone (hydrochloride, m.p. 176°), readily hydrolysed to 2 : 4-diketo-3-allyltetrahydrothiazole [5-benzylidene derivative (I), m.p. 88°]. Diallylthiocarbamide and $CH_2Cl \cdot COCl$ (II) in $COMe_2-C_6H_5N$ afford 2-allylimino-3-allyl-4-thiazolidone, an oil at -10°, the 5-benzylidene derivative, m.p. 53°, of which is hydrolysed (50% H_2SO_4) to (I) and allylamine. N-Phenyl-N'-allylthiocarbamide and (II) similarly give 2-allylimino-3-phenyl-4-thiazolidone, m.p. 151° [5-benzylidene derivative, m.p. 141°, hydrolysed (50% H_2SO_4 at 140°) to 2 : 4-diketo-3-phenyl-5-benzylidenetetrahydrothiazole (III), m.p. 208°]. The Na salt of 2-anilo-4-thiazolidone (?) with EtOH-allyl iodide yields 95% of 2-N-allylanilino-, m.p. 92° (5-benzylidene derivative, m.p. 165°), and 5% of 2-anilo-3-allyl-4-thiazolidone [5-benzylidene derivative, m.p. 106.5°, hydrolysed to (I) and NH_2Ph]. N-Benzoyl-N'-p-bromophenylthiocarbamide and (II) afford 2-benzoylimino-3-p-bromophenyl-4-thiazolidone, m.p. 213° [5-benzylidene derivative, m.p. 253°, hydrolysed (60% H_2SO_4 at 160°) to 2 : 4-diketo-3-p-bromophenyl-5-benzylidenetetrahydrothiazole, m.p. 247°], which is hydrolysed by dil. alkali to N-benzoyl-N'-p-bromophenylthiocarbamide, m.p. 233—234° (decomp.), and by conc. HCl to 2 : 4-diketo-3-p-bromophenyltetrahydrothiazole, m.p. 163°. Contrary to Dixon and Kennedy (J.C.S., 1920, 117, 74), $NHPh \cdot CS \cdot NH \cdot CO_2Et$ and (II) in $C_6H_6-C_6H_5N$ give 2-carbomethoxyimino-3-phenyl-4-thiazolidone, m.p. 256° (slow decomp. >230°) [5-benzylidene derivative, m.p. 225°, hydrolysed to (III)], which is hydrolysed (acid; alkali causes disruption) to 2 : 4-diketo-3-phenyltetrahydrothiazole. Contrary to Wheeler and Johnson (A., 1902, i, 760), $CHClPh \cdot CO_2Et$ and $NH_2 \cdot CS \cdot NHPh$ furnish 2-anilo-5-phenyl-4-thiazolidone (IV), m.p. 185°, hydrolysed (40% H_2SO_4 at 140°) to a 1 : 2 mixture of 2 : 4-diketo-5-phenyl-, m.p. 130°, and -3 : 5-diphenyl-, m.p. 173°, -tetrahydrothiazole, which result thus : (IV) \rightarrow thiohydantoic acid, which then loses either NH_3 or NH_2Ph with subsequent ring closure. Methylation of the Na salt of (IV) gives 2-N-methylanilino-5-phenyl-4-thiazolidone, m.p. 144°, also prepared from $CHBrPh \cdot CO_2Et$ and $NH_2 \cdot CS \cdot NPhMe$. $CClPh_2 \cdot CO \cdot NHPh$ and NH_4CNS in $COMe_2$ give (unexpectedly) 4-keto-2-thion-3 : 5 : 5-triphenyltetrahydroglyoxaline, m.p. 254°, which affords a S-Me ether, m.p. 143°, and is converted by conc. HNO_3 into the 2 : 4-diketo-derivative, m.p. 203.5°, also prepared from benzoic acid and $NH_2 \cdot CO \cdot NHPh$ at 180—190°. 2-Anilo-5 : 5-diphenyl-4-thiazolidone, m.p. 253° [obtained (cf. Wheeler and Johnson, loc. cit.) from NH_2Ph and $CNS \cdot CPh_2 \cdot CO_2Et$ (?)], is methylated (using Na salt) to 2-N-methylanilino-, m.p. 191°, and

2-anilo-3-methyl- (V), m.p. 134°, -5:5-diphenyl-4-thiazolidone. (V) is hydrolysed to 2:4-diketo-5:5-diphenyl-3-methyltetrahydrothiazole, m.p. 102°. $\text{CClPh}_2 \cdot \text{COCl}$ and $\text{NHPh} \cdot \text{CS} \cdot \text{NHMe}$ in C_6H_6 - $\text{C}_6\text{H}_5\text{N}$ give 25% of (V) and 75% of 2-methylimino-3:5:5-triphenyl-4-thiazolidone, m.p. 119° (hydrolysed to NH_2Me and 2:4-diketo-3:5:5-triphenyltetrahydrothiazole, m.p. 150°), the only case (so far noted) of the production of two isomerides in such a reaction.

H. B.

Action of formaldehyde on cysteine. S. RATNER and H. T. CLARKE (J. Amer. Chem. Soc., 1937, 59, 200—206).—Cysteine (I) reacts with aq. CH_2O over a wide range of p_{H} (very rapidly if > 5) to give (cf. Schubert, A., 1936, 824) *thiazolidine-4-carboxylic acid* (II), m.p. 196—197° (decomp.), $[\alpha]_{\text{D}}^{20} -141^\circ$ in H_2O [hydrochloride, m.p. 184—185° (decomp.)]; *Me ester*, b.p. 75°/1 mm. (hydrochloride, decomp. 164—165°), which behaves as an ampholyte. (II) is not affected to any appreciable extent by N-HCl at 100° [some hydrolysis to (I) and CH_2O is shown by distillation], but with $\text{CH}_2\text{I} \cdot \text{CO}_2\text{H}$ and CH_2PhCl in aq. K_2CO_3 at room temp. *S*-carboxymethyl- and *S*-benzyl-cysteine, respectively, are produced. (II) is oxidised (air in a solution of p_{H} 10.2 containing a little FeCl_3 ; aq. H_2O_2 ; I-KI) to cystine, whilst Br in aq. AcOH gives cysteic acid. (II) is also converted into (I) by Na_2SO_3 ; reaction is rapid at p_{H} 5. *Acetylthiazolidine-4-carboxylic acid*, m.p. 143.5—144.5°, $[\alpha]_{\text{D}}^{20} -133.5^\circ$ in H_2O , is oxidised by H_2O_2 (not I) to the *sulphoxide*, m.p. 188—190° (decomp.), or *sulphone*, m.p. 190° (decomp.). *N*- β -Thiolethylphthalimide is hydrolysed (20% HCl) to $\text{SH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \cdot \text{HCl}$, which with aq. CH_2O gives *thiazolidine*, b.p. 164—165° [hydrochloride, m.p. 180° (decomp.)]; *Ac derivative*, b.p. 83—85°/0.7 mm. (sulphone, m.p. 122°); this is oxidised by I-KI to $(\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{S})_2$ and by Br-aq. AcOH to taurine.

H. B.

Cyanine dye series. VIII. Dyes derived from 1-methylphenanthro-[9:10]-thiazole. G. H. KEYES and L. G. S. BROOKER (J. Amer. Chem. Soc., 1937, 59, 74—79).—9-Acetamidophenanthrene, m.p. 213—215° (lit. 207—208°) (modified prep.), and P_2S_5 in PhMe with a little $\text{C}_6\text{H}_5\text{N}$ give 9-thioacetamidophenanthrene, m.p. 181—182° (decomp.), oxidised $[\text{K}_3\text{Fe}(\text{CN})_6]$, dil. NaOH] to 1-methylphenanthro-[9:10]-thiazole, m.p. 145—147° [methiodide, m.p. 206—208° (decomp.)], and ethiodide, m.p. 202—204° (decomp.), prepared through the metho- (I) and etho- (II) *p*-toluenesulphonate, respectively]. 2-Iodoquinoline ethiodide with (I) and (II) in $\text{EtOH} \cdot \text{NEt}_3$ gives 2-methyl-1'-ethyl-, m.p. 244—246° (decomp.), and 2:1'-diethyl-, m.p. 248—250° (decomp.), -3:4:5:6-dibenzothia-2'-cyanine iodide, respectively, whilst (II) with quinoline ethiodide (III) (in $\text{EtOH} \cdot \text{KOH}$) and $\text{CH}(\text{OEt})_2$ (in $\text{C}_6\text{H}_5\text{N}$; followed by KBr) affords 2:1'-diethyl-3:4:5:6-dibenzothia-4'-cyanine iodide, m.p. 244—247° (decomp.), and 2:2'-diethyl-3:4:5:6:3':4':5':6'-tetrabenzothiacarbocyanine bromide, m.p. 200—202° (decomp.), respectively. These new dyes are not powerful sensitizers; they show absorption nearer the red than the corresponding compounds derived from methylnaphththiazoles. 2:1'-Diethyl-3:4-, m.p. 248—250° (decomp.), and

-5:6-, m.p. 285—288° (decomp.), -benzothia-4'-cyanine iodides are prepared from (III) and the requisite 1-methylnaphththiazole etho-*p*-toluenesulphonate in $\text{EtOH} \cdot \text{KOH}$. Improved preps. of 2:1'-diethylthia-4'-cyanine and 2:2'-diethyl-3:4- and -5:6-benzothia-2'-cyanine iodides are given. Absorption curves of most of the above dyes are given.

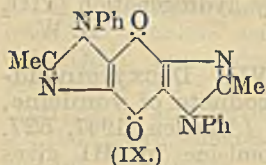
H. B.

Hydrogenation of vitamin- B_1 .—See A., III, 103.

Dicyclic compounds and their analogy with naphthalene. V. Benzthiodiazoles (phenylene-diazosulphides). K. FRIES and H. REITZ (Annalen 1936, 527, 38—60; cf. A., 1927, 779).—Benzthiodiazole (I) is definitely naphthoid in character. Addition of KNO_3 to its solution in conc. H_2SO_4 whereby the temp. ultimately attains 110° gives 4-nitrobenzthiodiazole (I), m.p. 95°, with small amounts of a substance, m.p. 104°; more drastic treatment causes rupture of the hetero-ring with formation of a very explosive diazonium compound which couples with *R* salt. (II) is reduced by SnCl_2 to 4-aminobenzthiodiazole, m.p. 136.5° (*Ac derivative*, m.p. 193°), which is converted in the usual manner into 4-hydroxybenzthiodiazole, m.p. 235° (*acetate*, m.p. 52°), transformed by Br in AcOH into 5:7-dibromo-4-hydroxybenzthiodiazole, m.p. 173° (decomp.) (*Na salt*; *acetate*, m.p. 157°), which is stable to light in $\text{C}_6\text{H}_5\text{N}$ or in NaOH containing CuSO_4 . The compound therefore differs markedly from 2:4- $\text{C}_{10}\text{H}_5\text{Br}_2\text{OH}$, the behaviour of which cannot therefore be attributed to peculiar modes of union in the nuclei. In attempted syntheses of (II), acet-*o*-nitroanilide (III) is converted by P_2S_5 at 100° into thioacet-*o*-nitroanilide (IV), m.p. 112°, which is oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution to the corresponding disulphide, m.p. 85°, reduced by Na_2S in alkaline solution to the initial material. Reduction of (III) or (IV) by NaHS in alkaline solution gives 1-hydroxy-2-methylbenziminazole, m.p. 231°. (I) is unaffected by Br in hot AcOH but is transformed by the halogen in presence of Fe at 100° into the *perbromide* $(\text{C}_6\text{H}_4\text{N}_2\text{S})_2 \cdot 2\text{HBr} \cdot \text{Br}_2$, m.p. 110° after softening at 80°. Reduction of 5-nitrobenzthiodiazole in EtOH by Sn and conc. HCl leads to 4-chloro-5-aminobenzthiodiazole (V), m.p. 169° (*Ac derivative*, m.p. 216°), whereas treatment with SnCl_2 and conc. HCl yields 5-aminobenzthiodiazole (VI), m.p. 95°, converted by Skraup's method into 5':6'-4:5-pyridinobenzthiodiazole, m.p. 115°. 4-Aminobenzthiodiazole (VII) similarly gives 2':3'-4:5-pyridinobenzthiodiazole, m.p. 141°, whereas (V) could not be caused to react, thus showing close analogy to the relationships in the C_{10}H_8 series. (VI) and (VII) couple directly in HCl to azo-dyes. The product from (VI) and diazotised $p\text{-NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ is reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to 4:5-diaminobenzthiodiazole, m.p. 158°, which with benzil in AcOH affords the quinoxaline, $\text{C}_{20}\text{H}_{12}\text{N}_4\text{S}$, m.p. 226° (decomp.). (VII) gives 4-amino-7-benzene-azobenzthiodiazole, m.p. $> 300^\circ$, whereas (V), like 1:2- $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{NH}_2$, does not couple. 2:2'-Dinitro-4:4':5:5'-tetramethoxydiphenyl 1:1'-disulphide is reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in alkaline solution to 5:6-dimethoxybenzthiodiazole, m.p. 142°, converted by H_2SO_4 into 5:6-dihydroxybenzthiodiazole, m.p. 249° (decomp.) (*Ac*₂ derivative, m.p. 120°), which, like

the "ββ"-dihydroxynaphthalenes, could not be oxidised to an *o*-quinone by HNO_3 or by PbO_2 in C_6H_6 or AcOH . Acetamidoquinol Me_2 ether is converted by P_2S_5 and K_2S in boiling PhMe into *thioacetamidoquinol* Me_2 ether, m.p. 101° , which is oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution to 4:7-dimethoxy-2-methylbenzthiazole (VIII), m.p. 101° , demethylated by $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ to 4:7-dihydroxy-2-methylbenzthiazole, m.p. 218° (sulphate, m.p. $>300^\circ$). This is oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ and dil. H_2SO_4 to 4:7-diketo-2-methyl-4:7-dihydrobenzthiazole, m.p. 159° (decomp.). Treatment of (VIII) with KOH in abs. EtOH at 110° followed by diazotisation gives 4:7-dimethoxybenzthiodiazole, m.p. 120° , converted by conc. HCl at 100° into 7-hydroxy-4-methoxybenzthiodiazole, m.p. 101° , and by fuming HCl at 115° into 4:7-dihydroxybenzthiodiazole, m.p. 233° (diacetate, m.p. 114°), which is oxidised by FeCl_3 to benzthiodiazole-4:7-quinone, m.p. 132° . This, with CaOCl_2 , possibly reacts initially in the same manner as α -naphthaquinone but the change is immediately followed by violent evolution of N_2 . 5:6-Dichloro-4:7-dihydroxybenzthiodiazole, m.p. 205° (decomp.), is unchanged by $\text{SnCl}_4\text{--AcOH}$ or NH_2Ph but is oxidised by FeCl_3 in boiling AcOH to 5:6-dichlorobenzthiodiazole-4:7-quinone, m.p. 237° (decomp.). This resembles the corresponding dichloronaphthaquinone since it is transformed by NH_2Ph in boiling EtOH into 6-chloro-5-anilinobenzthiodiazole-4:7-quinone, m.p. 216° , the NO -derivative, m.p. 228° (decomp.), of which is transformed by NH_2Ph at 100° into 5:6-dianilinobenzthiodiazole, m.p. $130\text{--}135^\circ$.

2:5-Dichloro-3:6-diacetamido-*p*-benzoquinone is transformed by NH_2Ph in boiling EtOH into 3:6-dianilino-2:5-diacetamido-*p*-benzoquinone (trihydrate, converted at 100° or by hot EtOH into the semihydrate), which when heated at 260° , boiled with $\text{NaOH}\text{--EtOH}$, or boiled with AcOH , PhNO_2 , or NH_2Ph passes into 1:1'-diphenyl-2:2'-dimethyl-4:5:4':5'-di-iminazolo-*p*-benzoquinone (IX), m.p. $>360^\circ$.



(IX.)

Production of furoyl-substituted thiolbenzthiazoles.—See B., 1937, 23.

Synthesis of hordenine. Y. RAOUL (Compt. rend., 1937, 204, 74—76).—Tyrosine at 250° in vac. gives tyramine, which with boiling 40% CH_2O containing HCO_2H in 10 hr. affords hordenine (50%); at room temp. the reaction takes a month and may represent the bio-mechanism.

J. L. D.

Tobacco alkaloids. X. Syntheses of l-anabasine and d-anabasine. E. SPÄTH and F. KESZTLER (Ber., 1937, 70, [B], 70—72).—Treatment of dl-anabasine (I) with 1:6:6'-dinitro-2:2'-diphenic acid in boiling MeOH leads to l-anabasine 1-dinitrodiphenate (I), m.p. $264.5\text{--}265^\circ$ (vac.), $[\alpha]_D^{25} -76.92^\circ$ in abs. MeOH , whence l-anabasine, $[\alpha]_D^{18} -82.45^\circ$ [dipicrate, m.p. $198\text{--}199.5^\circ$ (decomp.)]. The mother-liquors from (I) yield d-anabasine d-dinitrodiphenate, m.p. $264\text{--}265^\circ$, $[\alpha]_D^{18} +76.22^\circ$ in abs. MeOH , whence d-anabasine, $[\alpha]_D^{18} +82.11^\circ$ (dipicrate, m.p. $198\text{--}199^\circ$). The dipicrate of (I) has m.p. $213\text{--}214^\circ$.

H. W.

Alkaloids from Arundo donax. L. J. MADINAVEITIA (Nature, 1937, 139, 27).—Donaxine with $\text{EtOH}\text{--KOH}$ and MeI in the cold, gives NMe_4I and a methoxymethylindole; with EtI an ethoxymethylindole is obtained. A cryst. alkaloid, $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2$, and an amorphous phenolic base, both indole derivatives, have been obtained from *A. donax*, L.

L. S. T.

Papaverine and Fröhde's reagent. U. KUBLI (Pharm. Acta Helv., 1935, 10, 156—157; Chem. Zentr., 1936, i, 1263).—Cryptopine-free papaverine (I) gives a colour reaction with the reagent, which therefore cannot be used to detect cryptopine in (I).

H. N. R.

Quinine salt, m.p. 199° , of glycerophosphoric acid.—See A., III., 70.

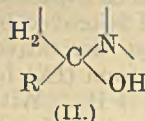
Quinine camphorsulphonates. L. NOBILI (G. Farm. Chim., 1935, 84, 232—239; Chem. Zentr., 1936, i, 2140).—The neutral, m.p. 210° , and basic, m.p. 192° , salts and their physiological action are described.

H. N. R.

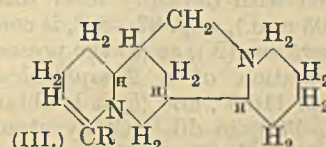
Niquine and niquidine. E. LÉGER (Bull. Soc. chim., 1937, [v], 4, 180—183).—Mainly polemical against Reyman *et al.* (A., 1936, 490). The author considers that δ -cinchonine is a dihydrocinchonine and niquine and niquidine are stereoisomeric forms of a dihydroquinine (A., 1920, i, 875).

J. W. B.

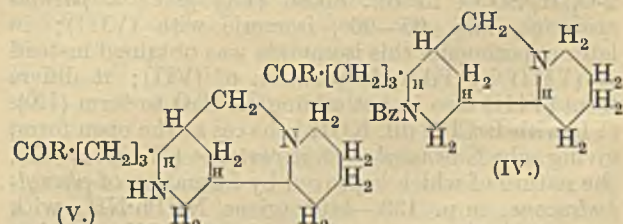
Lupin alkaloids. XII. Behaviour of lupanine towards Grignard reagents. K. WINTERFELD and E. HOFFMANN (Arch. Pharm., 1937, 275, 5—27; cf. A., 1936, 216).—The presence of a lactam group in lupanine (I) is proved by quant. reaction with Grignard reagents (2—3 mols.) in Et_2O to form additive products, hydrolysed to alcohols (II), which are too unstable to be isolated and readily lose H_2O to give substituted dehydrosparteines (III). The presence of the C:C:N linking in the dehydro-compounds is proved by benzoylation of the Et compound, which gives (IV) by ring-fission. The crude alkyldehydrosparteines (III) undergo fission of ring 1 in acid solution, giving alkylsparteones (V). This fission is much more facile if $\text{R} = \text{Ph}$ and various substances derived from this sparteone are prepared. Hydrogenation of (III) is the more rapid the lower is the mol. wt. of R. (I) and MgMeI give a red, un-



(II.)



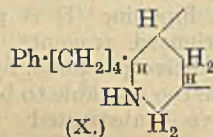
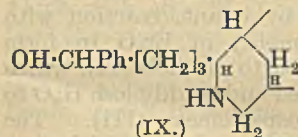
(III.)



(V.)

saturated, uncrystallisable oil, which, when distilled at $135^\circ/0.1\text{ mm.}$, gives H_2O and methyldehydrosparteine,

an unstable oil ($HgCl_2$ -compound, decomp. $257-258^\circ$; *diauri*-, decomp. 142° , and *platini*-chloride, decomp. $246-250^\circ$), hydrogenated ($Pd-CaCO_3$; $1H_2$) in abs. MeOH to *methylsparteine*, b.p. $117^\circ/0.8$ mm., m.p. $48-50^\circ$ ($HgCl_2$ -compound, decomp. 215° ; *diaurichloride*, $+H_2O$, decomp. 178° ; *picrate*, $+H_2O$, m.p. 221° ; *sulphate*, m.p. $122-123^\circ$; unchanged by H_2-PtO_2 in HCl or by $BzCl$ in dil. alkali). (I) and $MgEtI$ give a crude oily mixture, which, when distilled at $125^\circ/0.018$ mm., gives *ethyldehydrosparteine* (VI), an oil [*picrate*, m.p. 140° (decomp.) after sintering at 132° ; *platini*-, $+H_2O$, m.p. 251° (decomp.) (a fraction, decomp. $237-239^\circ$, was also obtained), and *diauri*-chloride, $+H_2O$, cryst.], hydrogenated ($Pd-CaCO_3$) to *ethylsparteine*, b.p. $109^\circ/0.004$ mm., m.p. $34-40^\circ$ ($HgCl_2$ -compound, $+H_2O$, decomp. 241° ; *diauri*-, decomp. 186° , and *platini*-chloride, forms, decomp. $257-258^\circ$, $264-265^\circ$, and $261-269^\circ$, respectively; *sulphate*, m.p. $124-125^\circ$). The alkylsparteines are probably mixtures of racemic or meso-forms, owing to the new asymmetric C formed; various possible types of such isomerism are discussed. (I) and $MgPhBr$ give a mixture, from which *phenyldehydrosparteine* (VII) [(III) ($R=Ph$)], m.p. $103-105^\circ$, b.p. $150-151^\circ/0.049$ mm. (*platinichloride*, decomp. 253°), gradually crystallises; with H_2-Pd this gives *phenylsparteine* (VIII), an oil, b.p. $160-161^\circ$ /high vac. When rubbed with H_2O , this gives a substance, $C_{21}H_{22}ON_2$, m.p. $79-80^\circ$ to a turbid liquid, clears at $139-140^\circ$, which may be a hydrate, but is probably ω -phenylsparteol (IX). The crude reaction product from (I) and $MgMeI$ or its distillation product gives with HBr the *dihydrobromide*,

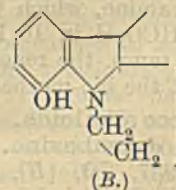
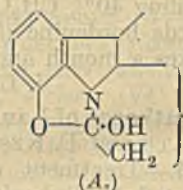


m.p. 248° , of ω -methylsparteone (V) ($R=Me$). Neutralisation of (VII) with dil. HCl or HBr and evaporation at 100° gives the *dihydrochloride*, m.p. $189-190^\circ$, and *dihydrobromide*, m.p. 210° , respectively, of ω -phenylsparteone (V) ($R=Ph$). In presence of PtO_2 and dil. HCl (VII) absorbs $2H_2$; it probably reacts in the open form (V), giving first (IX) and then the olefine by loss of H_2O ; the final product (isolated with difficulty after distillation at $180-181^\circ/0.03$ mm.), m.p. $87-88^\circ$, is considered to be ω -phenylsparteane (X), as (a) the presence of NH is proved by formation of a 2-naphthalenesulphonyl derivative, m.p. 116.5° , and (b) it is obtained also from (IX) by H_2-PtO_2 in dil. HCl by absorption of $1H_2$. With $2-C_{10}H_7 \cdot SO_2Cl$ in dil. alkali (IX) gives a *phenylsparteine*, m.p. $95-96^\circ$, isomeric with (VIII); in later experiments this isomerism was obtained instead of (VIII) by Pd -hydrogenation of (VII); it differs from (VIII) also in not adding on H_2O to form (IX). (VI) with $BzCl$ in dil. KOH behaves as the open form, giving oily *N*-benzoyl- ω -ethylsparteone (IV) ($R=Et$), the nature of which is proved by formation of *phenylhydrazone*, m.p. $139-140^\circ$ (gives $NHPh \cdot NH_2$ with conc. HCl), liberation of 1 mol. of $BzOH$ with hot 15% HCl, and formation of $PhCN$ by the von Braun reaction with PBr_5 .

R. S. C.

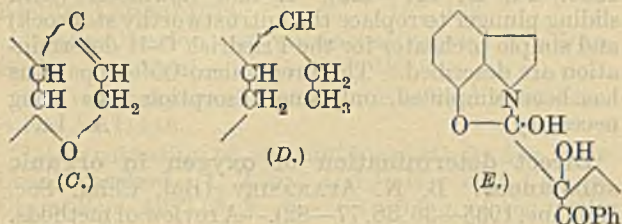
Strychnos alkaloids. XVI. 11-Amino- and 11-hydroxy-brucine. H. WIELAND and H. MAHLER-WEIN (Annalen, 1937, 527, 141-151).—Reduction of oximinobrucine with Zn dust and HCl gives 11-amino-brucine *dihydrochloride* (I), decomp. about 230° , converted by aq. NH_3 into the unstable 11-aminobrucine (II), m.p. 169° . The freshly-prepared nitrosoamine of oximinodihydrobrucic acid is reduced by $2N-NaOH$ and Zn dust to 11-aminodihydrobrucine (III), m.p. 224° [*hydrochloride*, darkens at 196° ; Bz_2 derivative, m.p. 225° , and its *hydrochloride*, m.p. 197° (decomp.)], also obtained by hydrogenation (PtO_2 in AcOH) of (II). Gradual addition of (III) to $SOCl_2$ at room temp. gives the base, $C_{23}H_{26}O_3N_3Cl$, m.p. $>300^\circ$ after darkening at 240° or (hydrated) m.p. 116° (decomp.) (*hydrochloride*). Addition of aq. $NaNO_2$ to (I) in H_2O gives the very stable 11-diazobrucine, m.p. 189° (decomp.) after softening at about 87° , the *hydrochloride* of which passes when warmed with dil. H_2SO_4 into 11-chlorobrucine (IV), m.p. 212° (decomp.) [*dihydrochloride* (V), m.p. $>300^\circ$; *methiodide*, m.p. 219° (decomp.)]. Hydrogenation of (V) (PtO_2 in AcOH- H_2O) gives *chlorodihydrobrucine*, m.p. 274° after darkening at 256° , and apparently an isomeric base, m.p. 212° , also obtained by hydrogenation of (IV). 11-Methoxybrucine, m.p. 192° (*hydrochloride* *methiodide*, incipient decomp. 236°), is obtained from (IV) and $NaOMe$ in boiling $NaOH$, whereby the possibility of isomerisation is not completely excluded. 11-Methoxydihydrobrucine has m.p. 237° (decomp.). The production of 11-hydroxybrucine, m.p. 178° [*hydrochloride* (VI), m.p. $>300^\circ$ (decomp.)], from the diazo-compound is successful only in the complete absence of Cl^- . 11-Hydroxydihydrobrucine, m.p. 233° (decomp.), is obtained by hydrogenation (PtO_2 in 50% AcOH) of (VI). H. W.

Strychnos alkaloids. XVII. Deoxyvomycin and other reduction products of vomicine. H. WIELAND and J. KEMMIG (Annalen, 1937, 527, 151-159).—Reduction of vomicine by HI gives deoxyvomycin I (I), m.p. 198° , $[\alpha]_D^{20} + 266.4^\circ$ in $CHCl_3$, isomerised by $NaOH$ in hot C_6H_5N into deoxyvomycin II (II), m.p. 207° , $[\alpha]_D^{20} + 231.4^\circ$ in $CHCl_3$. (II) but not (I) is electrolytically reduced at a Pb cathode to deoxyvomycin (III), m.p. 227° (Bz derivative, m.p. 190°), a phenolic base sol. in alkali and converted by acid oxidants into a red-violet dye, thus establishing the partial relationships



(A) and (B) for (I) and (III). In addition to O of OH, (III), like other *Strychnos* alkaloids, probably contains a bridge O, since it is converted by HI into iododihydrodeoxyvomycin, $C_{22}H_{22}ON_2I$, decomp. $>240^\circ$ (*hydriodide*), from which I could not be removed in the desired manner. (I) is catalytically hydrogenated with removal of bridge O to the bases $C_{22}H_{28}O_2N_2$ (IV) and $C_{22}H_{30}O_2N_2$ (V), which are

closely related, since (IV) is transformed into (V) by hydrogenation at increased temp. and pressure. Further (IV) and (V) are electrolytically reduced to the bases $C_{22}H_{30}ON_2$, m.p. 217°, and $C_{22}H_{32}ON_2$, m.p. 220—222°; the remaining O is present in phenolic OH. Both bases give on oxidation the dark red-violet colour characteristic of all derivatives of vomidine. It is therefore established that the hydrogenation of (I) to (IV) involves the saturation of the double linking and the opening of the O-bridge



(C \rightarrow D). The view is expressed that vomicine does not contain a *tert.* OH, but that the fourth O is present in a bridge.

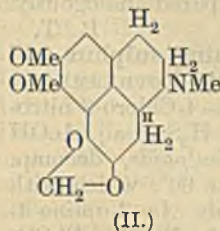
Gradual addition of 50% KOH to a boiling suspension of dihydrovomicine and PhCHO in abs. EtOH yields *benzylidenedihydrovomicine*, $C_{29}H_{30}O_4N_2$, m.p. 285° (decomp.), which does not dissolve in dil. mineral acids and is oxidised by $KMnO_4$ in $COMe_3$ -AcOH to the (?) hydrated base, $C_{28}H_{30}O_6N_2$ (cf. E), m.p. about 180° (decomp.), which passes when heated into a substance, m.p. 274°. H. W.

Alkaloids of *Senecio*. J. J. BLACKIE (Pharm. J., 1937, 138, 102—104; cf. A., 1936, 1002).—To EtOH *S. isatideus* yields *isatidine*, $C_{18}H_{25}O_7N$ (hydrolysed to *isatineic acid*, $C_{10}H_{16}O_6$, and *isatinecine*, $C_8H_{13}O_3N$), and *retrorsine*, also isolated from *S. glaberrimus* and *S. venosus*. *S. jacobaea* yields a base, $C_{18}H_{25}O_5N$, and *jacobine*, $C_{18}H_{26}O_6N$ (cf. Manske, A., 1932, 286), which is also isolated from *S. cineraria* and *S. erucifolius*. *S. palustris* yields a base, $C_{18}H_{25}O_5N$, m.p. 169°, and *S. sylvaticus*, *silvasenecine*. *S. saracenicus* yields three bases, C_5H_9ON , $C_8H_{13}ON$, and $C_{13}H_{21}O_3N$, and from *S. campestris*, *campestrine*, $C_{13}H_{19}ON$, m.p. 93°, and a base, m.p. 215°, are isolated. J. D. R.

Chemistry of mu-fang-chi. K. K. CHEN and A. L. CHEN (Chinese J. Physiol., 1937, 11, 25—28).—*Thunbergin*, $C_{20}H_{14}O_9$, m.p. 277—277.5°, and *mufang-chine*, $C_{14}H_{21}O_{11}N_{14}$, m.p. 231.5°, have been isolated from mu-fang-chi (probably the root of *Cocculus thunbergii*). E. M. W.

Constitution and synthesis of domesticine methyl ether (*d-epidicentrine*). Z. KITASATO and H. SNISHIDO (Annalen, 1937, 527, 176—182).—6 : 7-Dimethoxy-1-piperonyl-2-methyltetrahydroisoquinoline, m.p. 122°, gives a *hydrochloride*, m.p. 224°, and a *picrate*, m.p. 206—208°. 6 : 7-Dimethoxy-6'-nitro-1-piperonyl-2-methyltetrahydroisoquinoline (I), m.p. 152°, its *hydroiodide*, m.p. 205—210° (decomp.), and *picrate*, m.p. 189°, are described. Reduction of (I) with $SnCl_2$ and conc. HCl in AcOH at 15° affords 6 : 7-dimethoxy-6'-amino-1-piperonyl-2-methyltetra-

hydroisoquinoline, m.p. 132° (*dihydrochloride*, m.p. 223°), which is diazotised and then reduced to *dl-epidicentrine* (II), m.p. 142° [*hydrochloride*, m.p. 265—270° (decomp.) after becoming discoloured at 255°; *picrate*, m.p. 202—204° (decomp.)]; *methosulphate*, m.p. 238°]. By the successive use of *d*- and *l*-tartaric acid in abs. EtOH (II) is resolved into



l- (III), m.p. 138—139°, $[\alpha]_D^{25} -101.31^\circ$ in $CHCl_3$, and *d-epidicentrine*, m.p. 139°, $[\alpha]_D^{25} +102.27^\circ$ in $CHCl_3$, identical with natural domesticine Me ether (IV). Admixture of equal proportions of (III) and (IV) leads to (II). H. W.

Curarine from calabash curare. H. WIELAND, W. KONZ, and R. SONDERHOFF (Annalen, 1937, 527, 160—168).—Prolonged fractional crystallisation of various salts of the crude material supplemented by adsorption methods leads to an amorphous but only slightly coloured *perchlorate* of greatly enhanced toxic action. The best results are obtained by fractional adsorption of the *reineckates*, whereby a very toxic alkaloid results which gives a cryst. *anthraquinone-2-sulphonate* (I) and thence a cryst. *picrate* (II). Assuming that (II) contains base : acid = 1 : 1 the formula of the former, named *toxiferine* (III) (from *Strychnos toxifera*), is $C_{25}H_{27}O_2N_3$ but (I) cannot be derived from a base of this composition. (III) gives a characteristic green colour with HNO_3 and blue colour with $K_2Cr_2O_7-H_2SO_4$. It does not appear to belong to the same alkaloidal group as tubacurarine. Phenolic OH or OMe is not present in (III) or in the crude mixtures from which it is extracted. (III) does not appear to be a quaternary NH_4 base since the chloride yields only a slightly alkaline solution when treated with Ag_2O . It is not affected by catalytic H_2 . Protocatechuic acid is isolated from the initial material, in which the presence of succinic acid could not be established. H. W.

Chemical incompatibility between yatrene and some mineral salts. V. LUCAS (Bol. Assoc. brasil. farm., 1935, 16, 204—206).—Yatrene forms insol. salts with $MgCO_3$, $Mg(OH)_2$ and with Ca, Ba, and Sr salts. CH. ABS. (r)

Nitro-arsines. I. *m*-Nitrophenyldichloro-arsine. D. A. ISAČESCU (Bul. Soc. Chim. România, 1936, 18, 131—134).— $m-NO_2-C_6H_4-AsO_3H_2$, HCl, and SO_2 at 100° give $m-NO_2-C_6H_4-AsCl_2$, m.p. 46°.

R. S. C.

Organo-arsenic compounds. II. **Arsenation of aniline.** Metallic arsanilates. P. S. YANG and C. P. LO (J. Chinese Chem. Soc., 1936, 4, 477—484).—The prep. of arsanilic acid [$H Ag$, $H Mg$, $H Hg$, $H (PbOH)_2$, $H Bi(OH)_3$, and ? $H Sb(OH)_3$ salts] is modified. The solubilities of the salts are recorded. R. S. C.

Aryl tin hydroxyl and halide compounds of the type $SnAr_3X$. K. A. KOTSCHESCHKOV, M. M. NADJ, and A. P. ALEXANDROV (J. Gen. Chem. Russ., 1936, 6, 1672—1675).— $SnPh_4$ and $SnCl_4$ (4 hr. at 205—210°, 3 hr. at 150—160°) yield $SnPh_3Cl$, converted by KOH in Et_2O into $SnPh_3OH$. Tri-*o*-, *m*-,

and *p*-tolylchlorostannane, and *tri-p*-tolylhydroxystannane, m.p. 108—109°, were prepared analogously.

R. T.

Aromatic compounds containing sulphur and arsenic. K. BURSCHKIES and M. ROTHERMUNDT (Ber., 1936, 69, [B], 2721—2724).—4-Chloro-3-nitrophenylarsinic acid is converted by H_2S in aq. AcOH into *As* 4-chloro-3-nitrophenyl disulphide, decomp. 220° after becoming discoloured at 60°, which with Na_2S in boiling EtOH- H_2O yields *As* 3-amino-4-thiolphenyl disulphide, transformed by Na_2CO_3 - $PbCO_3$ into 3-amino-4-thiolphenylarsinic acid (I). (I) dissolved in *N*-NaOH is reduced by H_3PO_2 or by $MgCl_2$ - $Na_2S_2O_4$ at 50—60° to 3:3'-diamino-4:4'-dithiolarsenobenzene, freely sol. in alkali but insol. in acid. Passage of air through a solution of (I) in 2*N*-NaOH gives 3:3'-diamino-4:4'-disulphidodiphenyl-1:1'-diarsinic acid; the corresponding Ac_2 derivative is reduced by $FeSO_4$ and NaOH at 40° to 3-acetamido-4-thiolphenylarsinic acid. The products are amorphous, almost colourless powders without definite m.p. They are considerably more toxic than the corresponding OH derivatives and are therapeutically unimportant.

H. W.

Properties of proteins as a function of their fine structure. S. J. VON PRZYLECKI (Monatsh., 1936, 69, 243—269; cf. A., 1936, 155, 619).—The chemical properties of proteins are determined by the character and position of the active groups of the constituent NH_2 -acids. 14 typical groups are enumerated. Compounds can be formed through these, with other substances by electrovalent, covalent, or co-ordination linkings. Of a no. of NH_2 -acids, only arginine and tyrosine react with amylose and dextrin, whilst the proportions in which they occur in proteins determine the reactivity of the latter towards polysaccharides. The nature of the co-ordinating groups and the stoichiometric and stereochemical relationships are discussed and the formation of electrovalent polysaccharide-protein compounds is described. Adsorption of proteins on hydrocarbons is due to attraction of the NH_2 -acid hydrocarbon chains by the surface. The formation of compounds between proteins and fatty acids, esters, phosphatides, cholesterol, purine bases, nucleosides, and nucleotides is discussed.

R. S.

Position of constitutional investigations of proteins. W. GRASSMANN (Angew. Chem., 1937, 50, 65—72).—A lecture.

J. W. S.

Artificial "lipo-proteins."—See A., III, 87.

***d*-Limonene tetrabromide as a reagent in Rast's micro-method for the determination of mol. wt. of organic compounds.** H. Y. FANG and P. P. T. SAH (J. Chinese Chem. Soc., 1936, 4, 429—431).—Mol. wt. determinations of $C_{10}H_{16}$, camphor, 2:4:6- $C_6H_2Br_3$ -OH, $BzOH$, and *m*- $C_6H_4(NO_2)_2$, using *d*-limonene tetrabromide (I) as solvent, gave an average cryoscopic const. for (I) of 30.70.

C. R. H.

Improved sodium fusion technique for volatile or difficultly decomposable liquids. A. S. MICELI (J. Chem. Educ., 1936, 13, 515).—The pellet of Na, supported on glass wool, is heated in the upper half of a 4-in. test-tube.

L. S. T.

Methods of quantitative organic analysis by hydrogenation applied to micro-analysis. (MILLE.) A. LACOURT (Compt. rend., 1936, 203, 1367—1369).—N, S, halogens, and O are determined with an error of $\pm 0.21\%$ using a modification of fer Meulen's apparatus (cf. A., 1934, 424).

J. L. D.

Microchemical technique. I. Micro-methoxyl and micro-carbon-hydrogen determination. E. V. WHITE and G. F. WRIGHT (Canad. J. Res., 1936, 14, B, 427—429).—A new flowmeter (with sliding plunger to replace the untrustworthy stopcock) and simple preheater for the Friedrich C-H determination are described. The Pregl micro-OMe apparatus has been simplified, only one absorption tube being necessary.

A. Lr.

Direct determination of oxygen in organic substances. B. N. AFANASIEV (Bul. Chim. Soc. Române, 1935—36, 38, 77—82).—A review of methods.

D. C. J.

Detection of halogens (chlorine, bromine) in organic compounds. L. ROSENTHALER (Z. anal. Chem., 1937, 108, 22—23).—The materials are burned alone or in EtOH, and the products of combustion sucked over cotton wool impregnated with a 1% solution of *p*- NMe_2 - C_6H_4 -CHO + $NHPh_2$. Halogen compounds produce a yellow colour.

J. S. A.

Determination of organic iodine. J. A. GAUTIER (J. Pharm. Chim., 1937, [viii], 25, 145—156).—The I-compound with boiling *N*-NaOH or aq. EtOH-KOH and Zn affords ZnI_2 which, when freed from excess of Zn and org. material, is oxidised with $KMnO_4$; the liberated I is titrated.

J. L. D.

Detection of sulphur and nitrogen in organic compounds. L. ROSENTHALER (Z. anal. Chem., 1937, 108, 24—26).—(a) The material is burned in a stream of air, which is passed through 1% aq. HIO_3 . S compounds form SO_2 , which produces a blue coloration. (b) The material is treated with PbO_2 , and the gases evolved are passed into sulphanilic acid. Acid amides, $CO(NH_2)_2$ and its derivatives, and NO_2 -compounds, but not aliphatic or aromatic amines, azo-compounds, or heterocyclic compounds, form HNO_2 , which may be detected by adding α - $C_{10}H_7$ -ONa.

J. S. A.

Application of sulphuric-perchloric acid method of destruction [of organic materials] to qualitative test for nitrogen. H. GAUDUCHON-TRUCHOT (Ann. Chim. Analyt., 1936, [iii], 18, 316—317).—The material is heated with conc. H_2SO_4 , and dil. (about 20%) $HClO_4$ is added until decolorisation is complete. The solution is then tested for NH_3 .

J. S. A.

Analysis of organic compounds containing nitrogen. I. Determination of nitro-compound-nitrogen by the method of alkaline fusion. E. V. ALEXEEVSKI and Z. E. GOLBRAICH (J. Appl. Chem. Russ., 1936, 9, 1535—1542).—A mixture of 0.2—0.4 g. of the NO_2 -compound with 4 g. of NaOH and 0.8—1 g. of Zn dust is heated at a dull red heat in an Fe tube through which air is being aspirated, and the NH_3 evolved is absorbed in standard H_2SO_4 . The reaction is represented: $2OH \cdot C_6H_4 \cdot NO_2 +$

$10\text{H}_2\text{O} \rightarrow 3\text{C} + 8\text{CO}_2 + 10\text{H}_2 + \text{CH}_4 + 2\text{NH}_3$. The method is not applicable to liquid or volatile substances.

R. T.

Shortening the time required for micro-Kjeldahl determinations in the apparatus of Parnas and Wagner. S. Z. BARTOSIEWICZ (Biochem. Z., 1936, 289, 55–56).—A pump is used in emptying and washing the distillation flask.

P. W. C.

Semi-micro-determination of nitrogen. Micro-Kjeldahl apparatus.—See A., I, 152, 153.

Determination of amino-nitrogen by Van Slyke's method.—See A., III, 108.

Micro-analysis of nitrous oxide and methane.—See A., I, 148.

Determination of organic bismuth by the Parr bomb method. C. TSENG and L. WANG (J. Chinese Chem. Soc., 1937, 5, 3–5).—0.1–0.2 g. of the finely powdered sample is mixed with 0.2 g. of lactose and 12 g. of Na_2O_2 and heated in a Parr bomb. The Bi is then determined as Bi_2S_3 .

R. S. B.

Systematic procedure for detection and separation of anions.—See A., I, 147.

Determination of anhydrides of carboxylic acids. D. M. SMITH and W. M. D. BRYANT (J. Amer. Chem. Soc., 1936, 58, 2452–2454).—The anhydride (I) (alone or in MeOH or COMe_2) is (a) titrated directly with 0.5N- MeOH-NaOMe and a separate sample is (b) titrated with 0.5N- NaOH in presence of $\text{C}_6\text{H}_5\text{N}$ [which accelerates hydrolysis of (I)] using phenolphthalein or thymol-blue (dissolved in COMe_2 or dioxan; not in alcohols). The equiv. difference, $b - a$, determines the amount of (I) even if free acid is initially present. Data for Ac_2O , $(\text{EtCO})_2\text{O}$, $(\text{CH}_2\text{CO})_2\text{O}$, BzO_2 and *n*-heptoic, maleic, glutaric, phthalic, camphoric, and furoic anhydrides are given. Readily hydrolysed esters and lactones (e.g., HCO_2Alk and δ -gluconolactone) if present lead to ambiguous results; β -methylumbelliferone (reacts as an acid), phthalide (inert), and coumarin (inert) do not interfere.

H. B.

Azides. VII. *m*-Chlorobenzazide as a reagent for the identification of amines. P. P. T. SAH and C. S. WU (J. Chinese Chem. Soc., 1936, 4, 513–517; cf. A., 1936, 1006).— $m\text{-C}_6\text{H}_4\text{ClCON}_3$ (modified prep.) is suitable for identification of primary amines. *m*-Chlorophenylcarbamides from the following are described: NH_2Ph , m.p. 187°, *o*-, m.p. 174–175°, *m*-, m.p. 247–248°, and $p\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$, m.p. 272–273° (decomp.), $p\text{-C}_6\text{H}_4\text{BrNH}_2$, m.p. 237–238°, 4-aminodiphenyl, m.p. 220–221°, *o*-, m.p. 189–190°, *m*-, m.p. 236–237°, and $p\text{-C}_6\text{H}_4\text{MeNH}_2$, m.p. 214–215°, 3-bromo-*p*-toluidine, m.p. 228–229°, *p*-xylydine, m.p. 224–225°, *o*-, m.p. 211–212°, *m*-, m.p. 284–285°, and $p\text{-NH}_2\text{-C}_6\text{H}_4\text{CO}_2\text{H}$, decomp. about 300°, benzidine, m.p. about 300°, α -, m.p. 251–252°, and $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$, m.p. 263–264°, NH_2Bz , m.p. 226–227°, and NHPh_2 , m.p. 133–134°.

R. S. C.

3 : 5-Dinitro-*o*-toluic acid as a reagent for the identification of amines. P. P. T. SAH and C. H. TIEN (J. Chinese Chem. Soc., 1936, 4, 490–495).—3 : 5-Dinitro-*o*-toluates of the following, prepared in abs. EtOH , are suitable for identification: *o*-, m.p.

157–158°, *m*-, m.p. 135–136°, and $p\text{-C}_6\text{H}_4\text{MeNH}_2$, m.p. 160–161°, α -, m.p. 180–181° (decomp.), and $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$, m.p. 136–137°, 4-aminodiphenyl, m.p. 165–166°, benzidine, m.p. 164–165°, $\text{C}_6\text{H}_5\text{N}$, m.p. 143–144°, quinoline, m.p. 135–136°, NHPhMe , m.p. 141–142°, NH_3 , m.p. 218–219°, $\text{CO}(\text{NH}_2)_2$, m.p. 189–190°, *p*-xylydine, m.p. 145–146°, $p\text{-C}_6\text{H}_4\text{ClNH}_2$, m.p. 122–123°, $p\text{-C}_6\text{H}_4\text{BrNH}_2$, m.p. 197–198°, *o*-, m.p. 180–181° (decomp.), and $p\text{-OH-C}_6\text{H}_4\text{NH}_2$, m.p. 201–202°, *o*-, m.p. 157–158°, *m*-, m.p. 150–151°, and $p\text{-NH}_2\text{-C}_6\text{H}_4\text{CO}_2\text{H}$, m.p. 175–176°. NPhMe_2 and the nitroanilines do not form such salts. R. S. C.

Semicarbazides. V. α -Naphthyl-, VI, β -Naphthyl-, VII, 3 : 5-Dinitrophenyl-semicarbazide as a reagent for identification of aldehydes and ketones. P. P. T. SAH and (V) S. H. CHIANG, (VI, VII) P. C. TAO (J. Chinese Chem. Soc., 1934, 4, 496–500, 501–505, 506–512; cf. A., 1936, 1005).— α - (I) and β -Naphthyl- (II) and 3 : 5-dinitrophenyl-semicarbazones (III), respectively, of the following are prepared: MeCHO , m.p. 161–162°, 176–178°, 160–162°, EtCHO , m.p. 137–139°, 147–148°, 145–146°, Pr^iCHO , m.p. 128–129°, 138–139°, 134–135°, Pr^nCHO , m.p. 157–158°, 137–138°, 148–149°, Bu^iCHO , m.p. 124–125°, 134–136°, —, $n\text{-C}_6\text{H}_{11}\text{CHO}$, m.p. 112–113°, 126–128°, 135–136°, $n\text{-C}_6\text{H}_{13}\text{CHO}$, m.p. 133–134°, 143.5–134.5° (!), 141–142°, $n\text{-C}_6\text{H}_{15}\text{CHO}$, m.p. 103–105°, 135–136°, —, $n\text{-C}_8\text{H}_{17}\text{CHO}$, m.p. 122–123°, 150–151°, 116–117°, $n\text{-C}_9\text{H}_{19}\text{CHO}$, m.p. 118–119°, 148.5–149.5°, —, PhCHO , m.p. 200–201°, 222–223°, 269–270°, *m*-, m.p. 221–222°, 205.5–206.5°, —, and $p\text{-NO}_2\text{-C}_6\text{H}_4\text{CHO}$, m.p. 257–258°, —, —, CHPh:CHCHO , m.p. 196–197°, 205.5–206.5°, —, $o\text{-OH-C}_6\text{H}_4\text{CHO}$, m.p. 213–214°, 202–203°, 244–245°, furfuraldehyde, m.p. 192–193°, 205–207°, 225–226°, COMe_2 , m.p. 175–176°, 192–193°, 212–213°, CHPh:CHCOMe , m.p. 222–223°, 198–199°, 225–226°, $\text{COMe-C}_6\text{H}_{13}\text{-}n$, m.p. 147–148°, 144.5–145.5°, —, COPhMe , m.p. 206–207°, 207–208°, 227–228°, $p\text{-C}_6\text{H}_4\text{MeCOMe}$, m.p. 228–229°, 255–256°, —, $m\text{-NO}_2\text{-C}_6\text{H}_4\text{COMe}$, m.p. 245–246°, —, —, COPh_2 , m.p. 174–175°, 181.5–182.5°, 121–122°, $\text{CH}_2\text{AcCO}_2\text{Et}$, m.p. 126–127°, 159–161°, —, lævulic acid, m.p. 204° (decomp.), 214–215°, —, Et , m.p. 157–158°, —, —, and $\text{CH}_2\text{Ph lævulate}$, m.p. 141–142°, 141–142°, —, CHPh:CHCOPh , m.p. 201–202°, —, —, COMeEt , m.p. —, 169–170°, 199–200°, and $p\text{-C}_6\text{H}_4\text{BrCOMe}$, m.p. —, 239–240°, —. (I) and (II), but not (III), are suitable for identification of CO-compounds, (II) less well in the aliphatic series.

R. S. C.

***o*-Bromobenzhydrazide as reagent for identification of aldehydes and ketones.** CHUNG H. KAO, CHENG H. KAO, C. W. TU, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1936, 3, 555–560).—*o*-Bromobenzhydrazide, m.p. 152°, prepared from $o\text{-C}_6\text{H}_4\text{BrCO}_2\text{Et}$ and N_2H_4 , gives the following *o*-bromobenzoylhydrazones: MeCHO , m.p. 156–157°, EtCHO , m.p. 174–175°, Pr^iCHO , m.p. 155–157°, Bu^iCHO , m.p. 153–155°, $n\text{-C}_5\text{H}_{11}\text{CHO}$, m.p. 130–131°, $n\text{-C}_6\text{H}_{13}\text{CHO}$, m.p. 140–141°, furfuraldehyde, m.p. 162–163°, PhCHO , m.p. 180–181°, *o*-, m.p. 176–178°, and $p\text{-OH-C}_6\text{H}_4\text{CHO}$, m.p. 253–254°, $m\text{-NO}_2\text{-C}_6\text{H}_4\text{CHO}$, m.p. 195–197°, *p*-homosalicyl-

aldehyde, m.p. 183—184°, COMe₂, m.p. 153—154°, styryl Me ketone, m.p. 139—140°, Me hexyl ketone, m.p. 154—155°, COMePh, m.p. 146—147°, *p*-C₆H₄Me·COMe, m.p. 137—138°, *p*-OMe·C₆H₄·COMe, m.p. 165—166°, *p*-C₆H₄Br·COMe, m.p. 175—176°, *m*-NO₂·C₆H₄·COMe, m.p. 180—182°, Et lævulate, m.p. 96—97°, and cyclopentanone, m.p. 160—161°.

F. R. S.

***o*-Nitrobenzhydrazide as reagent for identification of aldehydes and ketones.** P. P. T. SAH and CHENG H. KAO (Sci. Rep. Nat. Tsing Hua Univ., 1936, 3, 461—468).—The *o*-nitrobenzhydrazones of the following have been prepared: EtCHO, m.p. 122—123°, PrⁿCHO, m.p. 136—137°, BuⁿCHO, m.p. 115—116°, *n*-C₅H₁₁·CHO, m.p. 119—120°, *n*-C₆H₁₃·CHO, m.p. 94—95°, *n*-C₇H₁₅·CHO, m.p. 98·5—99·5°, *n*-C₈H₁₇·CHO, m.p. 116·5—117·5°, *n*-C₉H₁₉·CHO, m.p. 103—104°, *m*-NO₂·C₆H₄·CHO, m.p. 202·2—203·2°, *p*-OH·C₆H₄·CHO, m.p. 257·5—258·5°, CHPh·CH·CHO, m.p. 200—201°, COMeEt, m.p. 175·4—176·4°, Me hexyl ketone, m.p. 67—68°, *p*-C₆H₄Me·COMe, m.p. 184—185°, *p*-C₆H₄Br·COMe, m.p. 228—229°, CPh₂, m.p. 184·4—185·4°, styryl Me ketone, m.p. 225—226°, lævulic acid, m.p. 176—177°, Et lævulate, m.p. 113·5—114·5°, and CH₂Ac·CO₂Et, m.p. 107·5—108·5°. The *m*-nitrobenzhydrazones of BuⁿCHO, m.p. 129·5—130·5°, *n*-C₆H₁₃·CHO, m.p. 114·5—115·5°, *n*-C₈H₁₇·CHO, m.p. 111—112°, and CHPh·CH·CHO, m.p. 197—198°, are also described.

F. R. S.

Phenylsemioxamazide (oxanilhydrazide) as reagent for identification of aldehydes and ketones. P. P. T. SAH and W. P. HAN (Sci. Rep. Nat. Tsing Hua Univ., 1936, 3, 468—476).—*Phenylsemioxamazones* of the following have been prepared: MeCHO, m.p. 231—232°, EtCHO, m.p. 215—216°, PrⁿCHO, m.p. 205—206°, BuⁿCHO, m.p. 201—202°, PrⁱCHO, m.p. 204—205°, *n*-C₅H₁₁·CHO, m.p. 196—197°, *n*-C₆H₁₃·CHO, m.p. 190—191°, *n*-C₇H₁₅·CHO, m.p. 193—194°, *n*-C₈H₁₇·CHO, m.p. 185—186°, *n*-C₉H₁₉·CHO, m.p. 184° (decomp.), COMeEt, m.p. 219—220°, Me hexyl ketone, m.p. 163—164°, CPh₂, m.p. 260—261°, CH₂Ac·CO₂Et, m.p. 162—163°, lævulic acid, m.p. 236° (decomp.), and CH₂Ph lævulate, m.p. 152—153°.

F. R. S.

Rapid approximate determination of aldehydes and ketones. IV. **Determination of benzaldehyde and acetone.** E. K. NIKITIN (J. Appl. Chem. Russ., 1936, 9, 2098—2108).—The concn. of PhCHO is derived from the time elapsing before appearance of turbidity after addition of KOH and COMe₂ to various dilutions of the solution in 25% EtOH. Conversely, the method is applicable to determination of COMe₂.

R. T.

Determination of semicarbazones. S. VEIBEL (J. Pharm. Chim., 1936, [viii], 24, 499—502).—Modifications of Harlay's method (A., 1936, 493) are suggested and its application to certain semicarbazones is discussed. The m.p. of the semicarbazide of AcCO₂H is 220—222° (slow heating), 246—248° (Maquenne block).

F. O. H.

Iodometric determination of salicylic acid, thymol, and β -naphthol. A. HEDE and S. STENSG (Dansk Tidsskr. Farm., 1937, 11, 13—17).—Practical details are given.

M. H. M. A.

Determination of salicylates. W. B. BRADLEY (Proc. Soc. Exp. Biol. Med., 1936, 35, 1—4).—A vol. (<10 c.c.) of solution containing 1—5 mg. of *o*-OH·C₆H₄·CO₂H is hydrolysed by heating at 100° with 1 drop of conc. aq. NaOH for 1 hr. and acidified with H₂SO₄. Preformed gas having been removed in the Van Slyke apparatus, 0·25—0·5 c.c. of saturated aq. NaBr saturated with Br is added and, after 1 min., 0·25—0·5 c.c. of saturated aq. KI. C₆H₅Br₃·OH is formed and the liberated CO₂ is measured. Results are accurate to $\pm 4\%$.

P. G. M.

Micro-determination of menthol, menthone, and menthyl ester and of the essential oil of *Mentha*. H. ULLRICH and M. SCHNEIDER (Z. physiol. Chem., 1937, 245, 181—184; cf. Bennet *et al.*, B., 1928, 68; Rehberg, A., 1925, i, 852).—The oil is steam-distilled from the plant (1—2 g.) and measured in a micro-burette, a correction being applied for the amount of oil remaining in the macro-burette in which the oil is first freed from H₂O. The menthone (I) content of the oil is determined by the NH₃OH method, the menthol is oxidised to (I) with CrO₃ + H₂SO₄, and the determination repeated. The menthyl ester is determined by saponification.

W. McC.

Determination of furfuraldehyde and hydroxymethylfurfuraldehyde with *p*-nitrophenylhydrazine. L. MAASKANT (Rec. trav. chim., 1936, 55, 1068—1070).—*p*-NO₂·C₆H₄·NH·NH₂ is preferred to phloroglucinol as a reagent for gravimetric determination.

F. N. W.

Cobalt colour reaction for detection of barbiturates. F. L. KOZELKA and H. J. TATUM (J. Pharm. Exp. Ther., 1937, 59, 54—62).—The Co-barbiturate colour is due to the presence of 1 or 2 NH groups and is stable with 2 NH over a wide, and with 1 NH over a narrow, range of *pH*. Compounds with >2 NH do not give the colour. The test can be used for determination of small amounts of barbiturates.

P. W. C.

Determination of some barbituric acid derivatives. K. KALINOWSKI (Wiadom. farm., 1935, 62, 633—635, 647—649; Chem. Zentr., 1936, i, 2391).—An argentometric method is described.

H. N. R.

Colorimetric determination of small quantities of morphine. C. G. VAN ARKEL (Pharm. Weekblad, 1937, 74, 134—137).—The method of Hofmann and Popovici (A., 1935, 877) has been studied. The colour intensity must be measured within 15 min. Codeine, thebaine, and meconic acid give no coloration, whilst narcotine, papaverine, and narceine give only an extremely weak blue one.

S. C.

Potentiometric titration of proteins and amino-acids. T. SODA and U. TANABE (J. Chem. Soc. Japan, 1935, 56, 672—682).—The Sb or quinhydrone-Pt electrode is used.

CH. ABS. (e)

Thiol groups in proteins. A. TODRICK and E. WALKER (Biochem. J., 1937, 31, 292—296).—The ·SH content of proteins is determined by measuring the amount of dichlorophenol-indophenol required for its oxidation. No free ·SH occurs in native serum-albumin (I) or ovalbumin (II) or in denatured (I), but denatured (II) contains the ·SH equiv. of 0·63% of cysteine and native myosin the equiv. of 0·27%.

W. McC.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

APRIL, 1937.



Hydrogen bridges in organic compounds. M. L. HUGGINS (J. Org. Chem., 1936, 1, 407—456).—A theoretical (non-mathematical) discussion of O·H·O (in carboxyl and in hydroxyl), N·H·O, N·H·N, C·H·N, C·H·O, and N·H·X bridges in org. compounds, with a full bibliography. In solid $\text{NHCl}(\text{CH}_2\text{Ph})_3$, the N, H (attached to N), and Cl atoms lie on threefold symmetry axes, suggesting $\text{N}\cdot\text{H}\cdots\text{Cl}$ bridges.

E. W. W.

Use of X-rays in the identification and estimation of mixtures of aliphatic compounds. S. H. PIPER (J.S.C.I., 1937, 56, 61—66T).—A lecture. The application of X-ray measurements to mixtures of aliphatic compounds shows that the chain length of many *iso*-acids is $>$ that of the supposedly corresponding normal acids and binary mixtures of the latter corresponding exactly with *iso*-acids are found. Even-numbered hydrocarbons in which the chain is tilted adopt a vertical chain form if melted or contaminated with a homologous impurity. The nature of binary (and to a smaller extent of ternary) mixtures is determined by a combination of mixed m.p. and X-ray spacings. It is thus proved that all naturally occurring hydrocarbons with >20 C have odd-numbered chains and that fractions apparently containing even-numbered chains are binary mixtures. Synthetic mixtures of alcohols agree in m.p. (and m.p. of derivatives) and X-ray spacing with those obtained from lac wax.

R. F. P.

Analysis of isotopic mixtures of deuteromethanes and ethanes by infra-red absorption spectra. W. S. BENEDICT, K. MORIKAWA, R. B. BARNES, and H. S. TAYLOR (J. Chem. Physics, 1937, 5, 1—9).—Infra-red absorption spectra of a no. of D-containing samples of CH_4 and a few of C_2H_6 have been investigated with a rock-salt spectrometer. The absorption of many "unknown" samples was determined, and several "standard" samples were prepared. CD_4 was prepared by reduction of CO by D_2 on a Ni catalyst and was slightly contaminated by CD_3H . The Grignard reaction using MeI and D_2O yielded MeD, spectroscopically free from CH_2D_2 but slightly contaminated by CH_4 . To prepare CH_2D_2 , CH_2I_2 was added dropwise to $\text{EtOD} + \text{D}_2\text{O} + \text{Zn}$ dust; the resulting gas contained a considerable amount of MeD and smaller amounts of CHD_3 and CH_4 . CHD_3 was prepared similarly using CHI_3 and CHCl_3 , but was considerably contaminated by CH_2D_2 , MeD, and CD_4 . All the observable fundamental frequencies of each methane isotope were identified, and the isotopic composition of the mixtures was calc. from the relative intensity of absorption at various characteristic λ .

W. R. A.

Mechanism of decomposition of ethane.—See A., I, 190.

Conjunct polymerisation. Influence of temperature, concentration, and quantity of sulphuric acid on polymerisation of olefines. V. N. IPATIEV and H. PINES (J. Org. Chem., 1936, 1, 464—489).—The report of Ormandy and Craven (B., 1927, 739) that amylene with excess of H_2SO_4 gives a product containing paraffins in the high- and olefines in the low-boiling fraction of the upper layer is not confirmed. *n*-Butene, mono- (I), di- (II), and tri-*isobutene* (III), *isopropylethylene*, nonene, and dodecene with excess of 96% H_2SO_4 at 0° give a hydrocarbon layer of which the fraction b.p. $225\text{—}250^\circ$ is free from olefines; the fraction of b.p. $>250^\circ$ contains 30% of olefines, with *cycloolefines* and saturated hydrocarbons. (II) and (III) give products of the same range of b.p., including octane and dodecane, indicating some depolymerisation. The yield of paraffins decreases as $[\text{H}_2\text{SO}_4]$, or ratio of H_2SO_4 to olefine, decreases. With (I), 96% H_2SO_4 gives a lower-boiling product than 87% H_2SO_4 , which yields mostly (III). 77% H_2SO_4 gives (II), (III), and tetra-*isobutene*; the last is the main product from (II) at 0° , but at 55° (III) is formed (depolymerisation). 67% H_2SO_4 does not polymerise (I) at 0° ; at 35° , (I), but not (II), is polymerised. 77% H_2SO_4 at 35° gives similar results to those at 0° . Distinction is drawn between "true" polymerisation, and "conjunct" polymerisation (by 96% H_2SO_4), involving conversion of alkyl esters into open-chain olefines or cyclic paraffins, the last being dehydrogenated to cyclic olefines, with simultaneous hydrogenation of olefines to paraffins.

(II) ($\beta\delta\delta$ -trimethyl- Δ^4 - and Δ^5 -pentene, b.p. $100\text{—}106^\circ$) was prepared by passing (I) over H_3PO_4 at $110\text{—}120^\circ$; for (III) the fraction of b.p. $176\text{—}178^\circ$ was used. Nonene, b.p. $130\text{—}135^\circ$, and dodecene, b.p. $190\text{—}200^\circ$, were similarly prepared from propene at $205^\circ/11$ atm. Analysis of olefine mixtures by treatment with H_2SO_4 or with Br is criticised. For analysis, hydrogenation with Ni at 160° and $\text{H}_2/100$ atm. is used, followed by org. analysis and determination of mol. wt. Alternatively olefines are separated from paraffins and naphthenes by adding C_6H_6 and 96% H_2SO_4 at 0° (which does not cause polymerisation, but gives an alkylated benzene), and treating the hydrocarbon layer with oleum, and analysing the upper layer remaining. Naphthenes and paraffins are differentiated by treatment with H_2 under pressure at 275° ($\text{NiO-Al}_2\text{O}_3$). High-boiling polymerides containing the Bu' group are recognised by adding

PhBu^r or C₆H₆ at 0°, and shaking with H₂SO₄, when *p*-C₆H₄Bu^r₂ is formed. E. W. W.

Preparation of catalysts.—See A., I, 192.

Mechanism of vinyl polymerisations.—See A., I, 190.

Stereoisomerism of unsaturated compounds. III. Preparation of *cis*- and *trans*-Δ⁸-octenes.

W. G. YOUNG, Z. JASAITIS, and L. LEVANAS (J. Amer. Chem. Soc., 1937, 59, 403–406).—*meso*-Octane-δ_ε-diol [dipropyl glycol] (I) (this vol., 3) [diacetate (II), b.p. 100°/5 mm.] and aq. ZnBr₂-HBr (saturated at 20°) give a mixture (A) of δδ-dibromooctane (III) (formed by a pinacol rearrangement) and dl-δ_ε-dibromooctane (IV), b.p. 84–84.5°/4.3 mm. Debromination (Zn-Cu, EtOH; method: Wilkinson, A., 1932, 40) of (A) affords a mixture (B) of octane [from (III)] and octene [from (IV)]; treatment of (B) with Br and subsequent fractionation gives (IV), which is also obtained from (II) and aq. HBr (saturated at 0°) at 0°. The diacetate, b.p. 110°/5.5 mm., m.p. 26°, of dl-octane-δ_ε-diol (*loc. cit.*) and aq. HBr similarly give *meso*-δ_ε-dibromooctane (V), b.p. 79–80°/4.3 mm. The configurations of (IV) and (V) are assigned from their rates of reaction with KI in MeOH at 75°. (IV) and (V) with Zn-Cu in EtOH afford *cis*-, b.p. 61.9°/97.4 mm., m.p. about –115°, and *trans*-, b.p. 62.9°/103 mm., m.p. about –105°, Δ⁸-octene, respectively. (I) and PI₃ in CS₂ give (probably) δ-iodooctane, b.p. 112–114°/47 mm.

H. B.

Addition of hydrogen fluoride to ethylene. C. E. SUN and C. H. SZE (J. Chinese Chem. Soc., 1937, 5, 1–2).—The energy of formation of EtF from C₂H₄ and HF calc. by the method previously used (A., 1936, 799) is 64.3 kg.-cal., i.e., > the heat of dissociation (61.0) of the C-C linking. Hence no addition occurs. J. W. B.

Stereoisomerides of chlorodibromoethylene. H. VAN DE WALLE (Bull. Soc. chim. Belg., 1936, 45, 726–729).—*cis*-CClBr·CHBr₂, b.p. 53.9°/40 mm., m.p. –80.0°, with Br in sunlight affords CHBr₂·CClBr₂, reduced by Zn in EtOH to a mixture of stereoisomerides in which *trans*-α-chloro-αβ-dibromoethylene, m.p. –52°, predominates; this is isolated by distillation in vac. with EtOH vapour. Distillation or long keeping converts the *trans*- into the *cis*-isomeride. J. D. R.

Addition of hydrogen bromide to allyl bromide in the presence of various substances. IV. Effect of ferromagnetic metals free from oxides. Catalytic action of ferromagnetic metals and oxygen. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1937, 12, 51–54).—40–60% yields of dibromopropanes containing 95–92% of CH₂(CH₂Br)₂ are obtained by addition of HBr to CH₂:CH·CH₂Br in the presence of freshly reduced Ni or Fe freed from oxides and with exclusion of air. The metals are not attacked, but Co is attacked by the HBr and has little effect, the main product being the normal product CHMeBr·CH₂Br (62%). J. W. B.

Oxidation of α-ray cuprene.—See A., I, 194.

Determination of primary alcohols by phthalisation in benzene. S. SABETAY and Y. R. NAVES

(Ann. Chim. Analyt., 1937, [iii], 19, 35–38).—0.5–2 g. of alcohol is esterified for 2 hr. with 2 g. of *o*-C₆H₄(CO)₂O in 2 c.c. of C₆H₆. 45 c.c. of H₂O + 5 c.c. of C₅H₅N are then added, and the solution heated for 10 min. The excess of *o*-C₆H₄(CO₂H)₂ and acid ester are then titrated back with KOH. Phenols do not esterify; *sec.* alcohols react incompletely. J. S. A.

Matsutake alcohol, C₈H₁₅O, b.p. 165–173° (4'-iododiphenylurethane, m.p. 165.6–166°), and octenol (4'-iododiphenylurethane, m.p. 158.5–159.3°).—See A., III, 107.

Stereochemistry of deuterium compounds. I. Optical rotation of methylhexyldeutero-carbinol [β-deuteroxyoctane]. L. YOUNG and C. W. PORTER (J. Amer. Chem. Soc., 1937, 59, 328–329).—(+)-Octan-β-ol (I), [α]_D²⁵₅₄₆₁ +7.68°, is acetylated (AcCl at room temp.) and the resulting acetate hydrolysed with (a) aq. EtOH-NaOH and (b) D₂O-EtOD-NaOD to (a) (I) (rotation unchanged showing absence of racemisation) and (b) β-deuteroxyoctane (II), [α]_D²⁵₅₄₆₁ +7.55°. Acetylation of (II) and subsequent hydrolysis (aq. EtOH-NaOH) gives (I) (original rotation).

H. B.

Oxidative fission of the C-C linking. R. CRUEGEE (Angew. Chem., 1937, 50, 153–155).—The oxidation of α-glycols by Pb(OAc)₄ follows the course $\text{OH}\cdot\text{C}\cdot\text{C}\cdot\text{OH} + \text{Pb}(\text{OAc})_4 \rightarrow \text{OH}\cdot\text{C}\cdot\text{CO}\cdot\text{Pb}(\text{OAc})_3 + \text{AcOH} \rightarrow \begin{array}{c} \text{C}\cdot\text{O} \\ | \\ \text{C}\cdot\text{O} \end{array} \text{Pb}(\text{OAc})_2 + \text{AcOH} \rightarrow \dots \text{O}\cdot\text{C}\cdot\text{C}\cdot\text{O}\dots + \text{Pb}(\text{OAc})_2 \rightarrow 2\text{C}\cdot\text{O}$. Fission does not depend on particular weakness in the C-C linking of glycols, but on the production of αδ-diradicals which decompose spontaneously. Fission of the C-C linking is discussed.

H. W.

Properties of unsaturated sulphones. J. BÖESEKEN and E. DE R. VAN ZUYDEWIJN (Proc. K. Akad. Wetensch. Amsterdam, 1937, 40, 23–28; cf. A., 1936, 587, 589).—The transition β → α-isoprene sulphone is reversible and does not take place via the hydrate. Acyclic sulphones do not show this isomerisation. Oxidation of β-unsaturated cyclic sulphones gives *cis*-diols with KMnO₄ and *trans*-diols with AcO₂H. Conductivity measurements with the *cis*-diol-H₃BO₃ complex show that the saturated sulphones are rigid and the unsaturated sulphones are highly strained. M. H. M. A.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system. IV. Activation by sulphonyl groups. V. Course of prototropic change in bis-sulphonylpropenes. E. ROTHSTEIN (J.C.S., 1937, 309–317, 317–320; cf. A., 1934, 762).—IV. Benzyl-Δ^β-propenylsulphone with Br in CCl₄ affords βγ-dibromo-α-benzylsulphonylpropane, m.p. 85–87°, which with C₅H₅N-C₆H₆ yields γ-bromo-α-benzylsulphonyl-Δ^α-propene (I), m.p. 95–97°; the Δ^β-isomeride (II), m.p. 151–152°, is obtained from CH₂Ph·SO₂Na and αγ-dibromopropene. βγ-Dichloro-α-benzylsulphonylpropane, b.p. 215–220°/3 mm., m.p. 65° (from benzylsulphonyl-Δ^α-propene and Cl₂ in CHCl₃), with C₅H₅N-C₆H₆ affords γ-chloro-α-benzylsulphonyl-Δ^α-propene, m.p. 75–76°. (I) with EtSNa in EtOH yields impure α-benzylsulphonylethylthiopropene (III), b.p.

190—196°/0.2 mm., oxidised (H_2O_2) to a mixture of α -benzylsulphonyl- γ -ethylsulphonyl- Δ^a - (IV), m.p. 105—107°, and Δ^b -propene (V), m.p. 137°, which may be separated by fractional crystallisation from C_6H_6 and EtOAc -petroleum, and are interconvertible by heating alone or in solvents, and α -benzylsulphonyl- $\beta\gamma$ (?)-bis(ethylsulphonyl)propane, m.p. 119—120°. α -Ethylsulphonyl- Δ^b -propene, b.p. 129°/11 mm. (from the sulphide with H_2O_2), with Br in CCl_4 - CHCl_3 yields $\beta\gamma$ -dibromo- α -ethylsulphonylpropane, b.p. 166°/0.6 mm., which with $\text{C}_5\text{H}_5\text{N}$ gives a mixture of mono- and di-bromides. γ -Chloro- β -hydroxy- α -benzylsulphonylpropane (VI), m.p. 97—98°, prepared by oxidation (H_2O_2 - AcOH) of the sulphide, b.p. 123°/0.05 mm. [from $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ (VII)], and EtSNa in MeOH give β -hydroxy- γ -ethylthio- α -benzylsulphonylpropane, b.p. 225°/0.5 mm. (slow decomp.), converted by PCl_5 in CHCl_3 into β -chloro- γ -ethylthio- α -benzylsulphonylpropane, m.p. 56—58°, which with boiling $\text{C}_6\text{H}_5\text{N}$ affords pure (III), b.p. 176°/0.02 mm., oxidised (H_2O_2) to a mixture of (IV) and (V). γ -Chloro- β -hydroxy- α -ethylsulphonylpropane, b.p. 141°/0.1 mm., m.p. 49°, prepared by oxidation (H_2O_2 - AcOH) of the sulphide (VIII), b.p. 100°/9 mm. [from EtSNa and (VII)], gives β -hydroxy- γ -benzylthio- α -ethylsulphonylpropane, b.p. 216°/0.3 mm., converted by PCl_5 in CHCl_3 into an oil, b.p. 220°/1.3 mm. (decomp.), which with boiling $\text{C}_6\text{H}_5\text{N}$ yields γ -benzylthio- α -ethylsulphonyl- Δ^a -propene, b.p. 171°/0.02 mm., oxidised (H_2O_2) to (III) and (IV). (VIII) in EtOH yields β -hydroxy- α -benzylthio- γ -ethylthiopropene (IX), b.p. 162—163°/0.2 mm., and [from unchanged (VII) in (VIII)] β -hydroxy- $\alpha\gamma$ -bis(benzylthio)propane, b.p. 215°/0.2 mm., oxidised to β -hydroxy- $\alpha\gamma$ -bis(benzylsulphonyl)propane, m.p. 204—205°. (IX) is oxidised (H_2O_2) to β -hydroxy- α -benzylsulphonyl- γ -ethylsulphonylpropane (X), m.p. 143—144°, and is converted by SOCl_2 in C_6H_6 into β -chloro- α -benzylthio- γ -ethylthiopropene, b.p. 144—145°/0.2 mm., oxidised (H_2O_2) to β -chloro- α -benzylsulphonyl- γ -ethylsulphonylpropane, m.p. 105—107°, also obtained from (X) by PCl_5 in CHCl_3 , converted by $\text{C}_5\text{H}_5\text{N}$ into (III) and (IV). EtSNa and $\text{Cl}\cdot[\text{CH}_2]_3\cdot\text{OH}$ in EtOH give γ -hydroxy-, b.p. 104°/15 mm., converted by SOCl_2 into γ -chloro-, b.p. 73°/14 mm., which affords γ -benzylthio- α -ethylthiopropene, b.p. 135°/0.3 mm., oxidised to γ -benzylsulphonyl- α -ethylsulphonylpropane, m.p. 153—154°, also obtained by catalytic reduction of (IV) and (V). $\text{EtS}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ is oxidised (H_2O_2) to Et ethylsulphonylacetate, b.p. 110°/0.3 mm., hydrolysed (HCl) to ethylsulphonylacetic acid (XI), m.p. 62—64°, decomposed at 240—250° to EtSO_2Me . Et benzylsulphonylacetate, m.p. 50°, is hydrolysed to the acid (XII), m.p. 139°, decomp. 180° to $\text{CH}_2\text{Ph}\cdot\text{SO}_2\text{Me}$. (IV) or (V) with PhCHO and $\text{C}_5\text{H}_{11}\text{N}$ afford $\beta\delta$ -benzylsulphonyl-ethylsulphonyl- α -phenylbutadiene, m.p. 154°, reduced (H_2) to a H_2 -compound, m.p. 124°. With O_3 , (IV) and (V) in H_2O - CHCl_3 yield $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CHO}$, $\text{EtSO}_2\cdot\text{CH}_2\cdot\text{CHO}$, (XI), and (XII), whilst (III) affords (X) and (XI).

V. $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{SEt})_2$ is oxidised (H_2O_2 - AcOH) to β -hydroxy- $\alpha\gamma$ -bis(ethylsulphonyl)propane (XIII), m.p. 113—114°, converted by PCl_5 into β -chloro- $\alpha\gamma$ -bis(ethylsulphonyl)propane, m.p. 81°, which with boiling $\text{C}_5\text{H}_5\text{N}$ affords $\alpha\gamma$ -bis(ethylsulphonyl)propene,

(XIV), m.p. 117—118°, converted by PhCHO into $\beta\delta$ -bis(ethylsulphonyl)- α -phenylbutadiene, m.p. 137—139°. (XIII) with Na and K alkoxides affords Na- and K-derivatives of a dimeride of (XIII), m.p. 95—98°, and with MeI and NaOEt gives a dimeride of $\alpha\gamma$ -bis(ethylsulphonyl)- α (?)-methylpropene, m.p. 160—161°. (IV) or (V) with Na or K alkoxides affords Na or K salts of the dimeride, m.p. about 88° (decomp.) (Me_4 derivative with MeI), or trimeride Me_3 derivative, m.p. about 65°, whilst with NaOMe and MeI, α -benzylsulphonyl- γ -ethylsulphonyldimethylpropene, m.p. 135—136°, is obtained. With KOMe, (X) affords a K-derivative of a dimeride, and (XIV) yields a dimeride, m.p. 95—98°. J. D. R.

Hydrolysis. F. ADICKES (Chem. Ztg., 1937, 61, 167—169; cf. A., 1927, 1169; 1928, 153; 1932, 1246; 1934, 509, 847, 849, 979; 1936, 598).—Published evidence for the theory that hydrolysis of carboxylic esters is preceded by addition of H_2O to the O of the CO group is discussed. R. C. M.

Catalytic decomposition of halogeno-acetic acids in the liquid phase. Action of sulphuric acid. J. B. SENDERENS (Compt. rend., 1937, 204, 209—211).— CO_2 and CO (% proportions indicated in parentheses) result from the decomp. of $\text{CCl}_3\cdot\text{CO}_2\text{H}$ at 135—165° in the presence of the following substances: $\text{Ca}_3(\text{PO}_4)_2$ (40, 60), animal charcoal (86, 14), CaCl_2 (45.5, 54.5), and conc. H_2SO_4 (48, 52), whilst with active C CHCl_3 and CO_2 result and ThO_2 or pumice afford HCl, CO_2 , and CO. Similarly $\text{CHCl}_2\cdot\text{CO}_2\text{H}$ affords HCl, CO_2 , and C with active C, and CO_2 and CO with $\text{Ca}_3(\text{PO}_4)_2$ (58, 42) or with ThO_2 -pumice (71, 29). With active C, $\text{CBr}_3\cdot\text{CO}_2\text{H}$ affords CHBr_3 and CO_2 , but $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ does not decompose. F. N. W.

β -Methyl- α -ethylvaleric acid. M. KONDAKOVA and M. KATZNELSON (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 403—404).—Contrary to the Tronov rule, better yields of $\text{CHMcEt}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$ are obtained from $\text{CHEt}(\text{CO}_2\text{Et})_2$ and *sec*-BuBr than from $\text{CHBu}(\text{CO}_2\text{Et})_2$ and EtI. The Cd salt is more sol. in H_2O (2.28 g. per 100 g. solution) than those of primary acids. A. Li.

Synthesis of glycerides of isooleic acid. A. BÖMER and J. STATHER (Fette u. Seifen, 1937, 44, 29—31).—Triisoolein, m.p. 36.8°, was obtained from Pb isooleate and tribromohydrin. α -isoOleo- α' - β -distearin, m.p. 57°, and α -isooleo- α' - β -dipalmitin, m.p. 46.5°, were synthesised via isopropylideneglycerol. F. C. B. M.

Determination of hydroxyl value of hydroxy-fatty acids. K. HINSBERG (Biochem. Z., 1937, 289, 294).—Addendum to a method previously described (A., 1936, 822). P. W. C.

Determination of free and esterified glyceric acid. S. RAPOPORT (Biochem. Z., 1937, 289, 406—410; cf. A., 1936, 58).—The colorimetric method of Eegriwe (cf. A., 1934, 171) modified by using dry material, increasing tenfold the concn. of the naphthoresorcinol reagent, employing the min. amount of conc. H_2SO_4 , and heating at 100° for 1 hr. gives accurate results in the determination of glyceric, mono- and di-phosphoglyceric acid (I), and serine.

(Cole) is feebly positive and not invariably reproducible. $\text{CHO} \cdot \text{CO}_2\text{H}$, if present in (I), is certainly not the main reducing agent of the solution and the hypothesis that (I) differs from normal $\text{H}_2\text{C}_2\text{O}_4$ only in respect of energy content is not disproved. H. W.

[Activated form of oxalic acid.] E. SCHRÖER (Ber., 1937, 70, [B], 411; cf. A., 1936, 1361, 1488).—In reply to Weber *et al.* (preceding abstract) it is very improbable that the activated form (I) of $\text{H}_2\text{C}_2\text{O}_4$ is merely the $\text{H}_2\text{C}_2\text{O}_4$ mol. with an extra supply of energy since it has a life period of about 24 hr. (I) is present in such minute amount that stoichiometric relationships are out of the question. H. W.

Simultaneous bilateral β -oxidation of dibasic fatty acids. C. ARTOM (Z. physiol. Chem., 1937, 245, 276—277; cf. Verkade *et al.*, A., 1936, 234).—The author's suggestion (Ann. Rev. Biochem., 1935, 4, 216) that β -oxidation may occur simultaneously at both ends of a chain has been proved correct by Mazza (cf. A., 1936, 1290). The frequent occurrence of Ac_2 in biological material also supports the suggestion. W. McC.

Mechanism of additive reactions. Chloro- and bromo- β -lactones from dimethylmaleic and dimethylfumaric acids. D. S. TARBELL and P. D. BARTLETT (J. Amer. Chem. Soc., 1937, 59, 407—410).—Na dimethylmaleate (I) and dimethylfumarate (II) with Cl_2 - H_2O give stereoisomeric β -lactones, m.p. 92—94° (III) and 141—142° (IV), respectively, of β -chloro- γ -hydroxybutane- β - γ -dicarboxylic acid (V), decomp. 173—174°, together with smaller amounts of (I), (III) and (IV) are both hydrolysed (10% H_2SO_4 at room temp.) to (V), different specimens of which react with aq. NaOH at 0° at the same rate. (I) and (II) with Br - H_2O similarly afford stereoisomeric β -lactones, m.p. 95—96° and 148—150°, respectively, of β -bromo- γ -hydroxybutane- β - γ -dicarboxylic acid, m.p. 168—170° (decomp.). (V) and aq. $\text{Ba}(\text{OH})_2$ at 0° give a little β - γ -oxidobutane- β - γ -dicarboxylic acid, m.p. 158—160° (decomp.). (III) and (IV) are not formed by addition of Cl_2 and subsequent elimination of NaCl from the resulting $(\text{CMeCl} \cdot \text{CO}_2\text{Na})_2$, since the Na salt of the known $(\text{CMeCl} \cdot \text{CO}_2\text{H})_2$ (Michael and Tissot, A., 1893, 142) undergoes slow decomp. in aq. solution at room temp. to chlorotiglic [β -chloro- α -methylcrotonic] acid (VI). The following two-stage mechanism for the production of (III) and (IV) is proposed: $(\text{CMe} \cdot \text{CO}_2^-) + \text{Cl}_2 \rightarrow \text{Cl}^- + \text{CO}_2 \cdot \text{CMeCl} \cdot \text{CMe} \cdot \text{CO}_2^- \rightarrow \text{CO} \text{---} \text{O}$. (VI) is also obtained when an aq. solution of the Na salt of (III) is heated. An additive compound of dimethylmaleic anhydride and Br could not be prepared in AcOH -HBr or CCl_4 (illumination causes evolution of HBr but the original anhydride is the only solid isolable). H. B.

Precipitation and colour reaction for ascorbic acid.—See A., III, 155.

Peculiarities of oxidation of vitamin-C.—See A., III, 155.

Action of diazomethane on formaldehyde. G. CARONNA (Gazzetta, 1936, 66, 772—775).— CH_2O and F^* (A., II.)

CH_2N_2 , stable at -3° , react slowly at 15° , and more rapidly at 30° . With $\text{CH}_2\text{O} + 2\text{CH}_2\text{N}_2$, no CH_2N_2 colour remains, and the aq. extract gives, with KOH -I, CHI_3 corresponding with a 28% yield of COMe_2 ; the formation of MeCHO is improbable, since $2\text{CH}_2\text{O} + 2\text{CH}_2\text{N}_2$ give the same amount of CHI_3 , and unchanged CH_2O . Traces of HCN and of MeNC are also formed. E. W. W.

Aldol condensations. IV. Dodecapentaenal from crotonaldehyde; dodecapentaenol and tetradecahexadecenoic acid. F. G. FISCHER, K. HULTZSCH, and W. FLAIG (Ber., 1937, 70, [B], 370—375).—The yield of straight-chain cryst. compounds from crotonaldehyde (I) in presence of piperidine (II) and AcOH increases when the reaction is rapidly performed and the subsequent distillation rapidly effected in a good high vac. The efficiency of the catalyst diminishes rapidly during the reaction owing to the irreversible reaction between (I) or its products and (II). Compounds of the Schiff base type such as dipiperidinomethane or benzyldenedipiperidyl behave similarly to (II) owing to fission in the acid solution but products from 1 mol. of (II) and ≤ 2 mols. of (I) are catalytically inactive. (I) gives dihydro-*o*-tolualdehyde, octatrienal, and dodecapentaenal (III), $\text{CH}_3 \cdot [\text{CH} \cdot \text{CH}]_5 \cdot \text{CHO}$, m.p. 166—167° (corr.), which gives a purple-red colour with SbCl_3 in CHCl_3 (semicarbazone, m.p. $>360^\circ$; oxime, m.p. $>360^\circ$; phenylhydrazone, m.p. 223°). (III) is hydrogenated to lauraldehyde (semicarbazone, m.p. 100°) and oxidised by Ag_2O in H_2O - EtOH to dodecapentaenoic acid, m.p. 240—245°, in poor yield. Reduction of (III) with $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH affords $\Delta^{10,11}$ -dodecapentaenol, m.p. 204° (corr.), which with SbCl_3 in CHCl_3 gives a wine-red colour, suddenly becoming blue. (III) and $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ at 50—60° and subsequently at 100° yield dodecapentaenylidenemalonic acid, m.p. 245—247° when placed in bath pre-heated to 240° (pyridinium salt), hydrogenated to *n*-dodecylmalonic acid, m.p. 120°, and transformed when heated into $\Delta^{10,11}$ -tetradecahexaenoic acid, m.p. 257—258° (decomp.) [*Et* ester, m.p. 174°, obtained from (III), $\text{CH}_2\text{Br} \cdot \text{CO}_2\text{Et}$, and Zn turnings]. H. W.

Preparation of 1:5-dioximes from pyridine bases. B. D. SHAW (J.C.S., 1937, 300—302).—Reduction (Na - EtOH) and treatment with $\text{NH}_2\text{OH} \cdot \text{HCl}$ of $\text{C}_5\text{H}_5\text{N}$ gives glutardialdoxime, converted into glutardialdehydebis-2:4-dinitrophenylhydrazone, m.p. 169—172°. From 2-picoline, 2:4:6-trimethylpyridine [nitrate, m.p. 199° (decomp.)] and 2-styrylpyridine are obtained respectively δ -acetaldehydebis-2:4-dinitrophenylhydrazone, m.p. 129°, α - γ -diacetyl- β -methylpropanedioxime, b.p. 275°/12 mm. (bis-2:4-dinitrophenylhydrazone, m.p. 197—199°), and ω -aldehyde- γ -keto- α -phenyl- Δ^2 -hexenedioxime (bis-2:4-dinitrophenylhydrazone, m.p. 55—59°). F. R. S.

Enolisation of sugars under the influence of different bases. A. M. KUZIN (Biochimia, 1936, 1, 101—112).—0.5*M*-Glucose in 0.5*N*- $\text{Ca}(\text{OH})_2$ at 25—30° (24 hr.) yields mannose, whilst in 0.5*N*- NaOH the chief product is fructose. The products obtained from glucose or fructose and $\text{Ca}(\text{OH})_2$ differ from those in NaOH in reducing I in KI in acid solution, and in giving colorations with FeCl_3 . It is supposed that

cyclic enols are formed with $\text{Ca}(\text{OH})_2$, and straight-chain enols with NaOH . R. T.

$\beta \rightarrow \alpha$ Conversion of fully acetylated sugars by alkali. M. L. WOLFROM and D. R. HUSTED (J. Amer. Chem. Soc., 1937, 59, 364—365).— β -*D*-Glucose, β -*D*-galactose, and β -*D*-mannose penta-acetates and β -lactose octa-acetate are converted into the α -forms (variable yields up to 50%) when solutions or suspensions in dioxan or Et_2O are shaken with solid NaOH in presence of a drying agent (CaSO_4 or Na) for 4—7 hr. Some deacetylation occurs. H. B.

Reagent for the copper-iodometric determination of very small amounts of sugar. M. SOMOGYI (J. Biol. Chem., 1937, 117, 771—776).—A reagent for the Cu-iodometric determination of sugars is described in which the reoxidation of Cu_2O by air is virtually eliminated by the presence of Na_2SO_4 . This enables very small amounts (0.01 mg. of glucose) to be determined accurately. The linear proportionality between the amounts of sugar and Cu reduced is established. The advantages of the $\text{K}_3\text{Fe}(\text{CN})_6$ reagents have been imparted to Cu reagents. P. W. C.

Reaction between sodium iodide and toluenesulphonyl derivatives of glucofuranose. D. J. BELL, E. FRIEDMANN, and S. WILLIAMSON (J.C.S., 1937, 252—253).—The additive product of glucofuranose 3:5:6-tribenzoate and CCl_4 , with p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_6\text{H}_5\text{N}$ affords β -methylglucosulphonate 3:5:6-tribenzoate 2-*p*-toluenesulphonate, m.p. 125—127°, $[\alpha]_D^{20}$ —61.9°. Similarly, 3:5-benzylideneisopropylidene-glucose, gives the 6-*p*-toluenesulphonate, m.p. 118°, $[\alpha]_D^{20}$ +14.2°, which with NaI in COMe_2 yields 6-iodo-3:5-benzylideneisopropylidene-glucose, m.p. 137°, $[\alpha]_D^{20}$ +17.7°. 3-Methylisopropylidene-glucose yields 6-chloro-3-methylisopropylidene-glucose 5-*p*-toluenesulphonate, m.p. 143°, $[\alpha]_D^{20}$ —46.6°.

J. D. R.

Formation of glucose hepta-acetate during acetolysis. K. FREUDENBERG and K. SOFF (Ber., 1937, 70, [B], 264—266).—The optical behaviour of α - (I) and β -methylglucoside tetra-acetate and glucose hepta-acetate (II) during acetolysis (Ac_2O - AcOH - H_2SO_4) combined with previous observations (A., 1933, 149) indicate the presence of (II) in the final mixtures. It is isolated in small amounts from the products of (I) and, in better yield, from those derived by short treatment of glucose with HCl - MeOH . H. W.

Determination of galactose by Hagedorn and Jensen's method.—See A., III, 162.

Determination of fructose with selenious acid. G. REIF (Z. Unters. Lebensm., 1937, 73, 20—26).—The distinctive test for ketoses previously described (A., 1936, 1154) is used as a basis for the determination. The wts. of Se formed when fructose (I), sucrose (II), glucose, galactose, lactose, and maltose are heated under specified conditions with H_2SeO_3 - H_2SO_4 of specified concn. are tabulated. Analyses of solutions of the mixed sugars agree closely with the vals. calc. from these tables. The amount of Se formed by the sugars examined other than (I) and (II) is extremely small. E. C. S.

Ketoheptose from *Sedum*.—See A., III, 107.

Cyanogenetic glucosides in Australian plants.

IV. *Zieria laevigata*. H. FINNEMORE and (MISS) J. H. COOPER. V. *Phyllanthus gastroemii*. H. FINNEMORE, (MISS) S. K. REICHARD, and (MISS) D. K. LARGE (J. Proc. Roy. Soc. New South Wales, 1936, 70, 175—182, 257—264).—IV. The flowering tops of *Z. laevigata* yield to COMe_2 *zierin*, the glucoside of $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}$, m.p. 156° after softening at 153°, $[\alpha]_D^{20}$ —29.5° [tetra- or penta-(?)acetate, m.p. 115—118°]; hydrolysis with emulsin yields HCN, glucose, and $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$.

V. The leaves of *P. gastroemii* yield to COMe_2 *phyllanthin*, the glucoside of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}$ (I) (tetra-acetate, m.p. 144°), hydrolysed by emulsin to HCN, glucose, and (I). J. D. R.

Chemical constitution of acacipetalin, a new cyanogenic glucoside from *Acacia lasiopetala*, Oliv., and *Acacia stolonifera*, Burch. C. RIMINGTON (South African J. Sci., 1935, 32, 154—171; Chem. Zentr., 1936, i, 2558—2559).—The inositol Me ether, *pinitol*, $\text{C}_7\text{H}_{14}\text{O}_6$, and a glucoside, *acacipetalin* (I), $\text{C}_{11}\text{H}_{17}\text{O}_6\text{N}$, m.p. 176.7°, $[\alpha]_D^{20}$ —36.6° in H_2O (tetra-acetate, m.p. 104°), are present. Alkaline, followed by acid, hydrolysis of (I) yields *D*-glucose and isobutyrylformic acid (2:4-dinitrophenylhydrazone, m.p. 188—191°) identical with a synthetic specimen from KMnO_4 oxidation of isobutyrideneacetone (2:4-dinitrophenylhydrazone, m.p. 163—165°); with 1% H_2SO_4 (I) yields HCN, *D*-glucose and $\text{Pr}^i\text{CO}_2\text{H}$. It is concluded that (I) is dimethylketen cyanohydrin β -glucoside. H. N. R.

Micro-determination of hexosans. S. M. STREPKOV (Biochem. Z., 1937, 289, 295—300).—Hexosans (mannan, galactan), freed from H_2O -sol. carbohydrates and starch, are boiled for 50 min. with 2% H_2SO_4 , neutralised with aq. NaOH , treated with 5% aq. $\text{Pb}(\text{OAc})_2$, filtered, and freed from Pb with H_2S . Total reducing substances are then determined by titration with 0.005*N*- $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.005*N*- $\text{Na}_2\text{S}_2\text{O}_3$ in a 2-c.c. sample of the filtrate. A second 2-c.c. sample is fermented with yeast after addition of Na_2HPO_4 and the reducing substances left after destruction of the hexoses are determined as before. Galactose (I), which is not attacked by yeast in the absence of $\text{PO}_4^{'''}$, is determined together with residual reducing substances in a third 2-c.c. sample after addition of yeast only. The mannose content is calc. from the difference between the first and third determinations and the (I) content from the difference between the third and the second. The hexosan contents are given by multiplying these vals. by 0.9 or from tables. When the concn. of reducing sugars is 80 mg. per 100 c.c. the error of the method is —0.9 to +2.1%. W. McC.

Structure of the crystallised components of cellulose. V. K. H. MEYER (Ber., 1937, 70, [B], 266—274).—Hydrocellulose, pptd. as artificial silk from solutions, has the same lattice as that obtained directly from ramie fibre by treatment with NaOH . Since the lattice is completely disrupted in solution it appears impossible to obtain by coagulation threads or crystallites in which all the chains are similarly

oriented. It must therefore be assumed that two oppositely directed systems of chains are concerned in the structure of the crystallites and hence also in those of native cellulose (I). A new model of the cellobiose residue and of the structural unit of (I) is therefore advanced. The evaluation of röntgenographic data in the elucidation of constitution and size of micelle and the limits of their predictions are discussed.

H. W.

Study of cellulose hydrolysis [by hydrochloric acid] by means of ethyl mercaptan. M. L. WOLFROM and L. W. GEORGES (J. Amer. Chem. Soc., 1937, 59, 282—286).—The course of the hydrolysis of cellulose (I) (concn. 5%) in fuming HCl at 16° is studied polarimetrically and by determination (from the S content) of the mol. size of the mercaptals (II) obtained (at various stages of the reaction) by treatment with EtSH. The (II) isolated at the approx. half-period correspond with the trisaccharide stage. Glucose Et₂ mercaptal (III) is first isolable when hydrolysis is about 66% complete. (III) is readily produced when *d*-glucose is shaken vigorously with EtSH (excess) in fuming HCl at 0°/15 min. The rate of hydrolysis (determined polarimetrically) of (I) by fuming HCl at 23° is the same as that using conc. HCl-ZnCl₂ (Hibbert and Percival, A., 1930, 1561). At an early stage of the hydrolysis, viz., $[\alpha]_D$ about +25°, final val. about +100°, the viscosity of the solution approaches that of an apparent equiv. amount of *d*-glucose.

H. B.

Catalytic synthesis of diethylamine. V. F. OROTZKI and A. B. DRANOVSKI (Ukrain. Chem. J., 1936, 11, 446—459).—The most active catalyst for conversion of 1 : 1 EtOH-NH₃ mixtures into NH₄Et₂ is Al₂O₃·SiO₂, at 340—360°, with a rate of flow of 1.2—1.4 litres of vapour per litre of catalyst per min. The yield of amines amounts to 30—40%, calc. on the EtOH used. Of the by-products, Et₂O, NH₂Et, and NEt₃, but not C₂H₄, can be returned to the reaction. The catalyst should be reactivated after 25—30 hr. of action, by passing steam at 350°.

R. T.

Closure and opening of the trimethyleneimine ring. C. MANNICH and G. BAUMGARTEN (Ber., 1937, 70, [B], 210—213).—Cl-amines containing Cl in *sec.* union in γ -position to NH₂ show no tendency towards formation of the trimethyleneimine ring whereas ring-closure occurs more or less readily if the halogen is in primary union. γ -Diethylamino- $\beta\beta$ -dimethylpropanol is transformed by SOCl₂ in CHCl₃ into α -chloro- γ -diethylamino- $\beta\beta$ -dimethylpropane (I), b.p. 81°/15 mm. (hygroscopic hydrochloride), in which Cl is readily replaced by NEt₂, NHPH, or CN. (I) is converted by NaI in COMe₂ at room temp. into diethyl- $\beta\beta$ -dimethyltrimethyleneammonium iodide, CMe₂< $\frac{\text{CH}_2}{\text{CH}_2}$ >NEt₂I, m.p. 180° (decomp.). The corresponding, very hygroscopic chloride (*aurichloride*, m.p. 143°; *platinichloride*, m.p. 190°) passes almost quantitatively at 190°/vac. into (I). Dimethyl- $\beta\beta$ -dimethyltrimethyleneammonium iodide, m.p. about 190° (decomp.), is derived from CH₂Cl·CMe₂·CH₂·NMe₂ (II) and NaI in COMe₂ or from *N*-methyl- $\beta\beta$ -dimethyltrimethyleneimine (III) and MeI in EtOAc; the corresponding, very hygroscopic chloride, m.p. about 165°

(*aurichloride*, m.p. 209°), gives (II) when distilled. NHMe·CH₂·CMe₂·CH₂·OH·HBr is transformed by HBr-AcOH at 165° into α -bromo- γ -methylamino- $\beta\beta$ -dimethylpropane hydrobromide, m.p. 181°, which when heated with KOH yields (III), b.p. 73—74° (hygroscopic hydrochloride, m.p. 150°; hydrobromide, m.p. 164—165°). α -Chloro- γ -piperidino- $\beta\beta$ -dimethylpropane, b.p. 115°/25 mm. (hydrochloride, m.p. 163°), obtained in good yield from γ -piperidino- $\beta\beta$ -dimethylpropanol, is transformed by NaI in COMe₂ into $\beta\beta$ -dimethyltrimethylenepiperidinium iodide (corresponding chloride, m.p. 155—160°). γ -Dimethylaminobutanol and SOCl₂ yield α -chloro- γ -dimethylaminobutane, b.p. 55°/14 mm. (hydrochloride; methiodide, m.p. 188°), converted by NaI in COMe₂ into dimethyl- α -methyltrimethyleneammonium iodide, m.p. 186—190° (decomp.); the very hygroscopic chloride gives an *aurichloride*, m.p. 228° (decomp.). H. W.

Pyrolysis of trimethyl-*n*-heptylammonium fluoride. C. L. TSENG, T. S. HO, and K. TUAN (Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 4, 9—16).—Trimethyl-*n*-heptylammonium fluoride, prepared from the hydroxide with HF, on pyrolysis yields dimethyl-*n*-heptylamine and (?) Δ^2 -heptene.

J. D. R.

Action of hexamethylenetetramine on alkyl halides in presence of monophenols. II. P. BOUCHEREAU (J. Pharm. Chim., 1937, [viii], 25, 159—173).—(CH₂)₆N₄ (I) with a large excess of boiling MeI containing PhOH affords (cf. A., 1936, 1502) an additive compound, decomp. 110—112°. Similarly with *o*-OH·C₆H₄·CO₂Na (II), a compound, decomp. 105—110°, is obtained. (I) and EtI afford with guaiacol, *p*-cresol, thymol, and (II) additive compounds, m.p. 120—130° (decomp.), resinifies when heated, resinifies when heated, and decomp. at 100°, respectively. (I) and amyl iodide afford with PhOH and (II) additive compounds, resinifying at 115° and stable to heat, respectively. (I), CH₂PhI, and (II) afford an additive compound. These compounds are stronger antiseptics than the constituent phenols, and are but slightly toxic.

J. L. D.

Chemistry in liquid sulphur dioxide. II. Substituted thionylidammonium compounds and thionylidquinolinium derivatives. K. WICKERT and G. JANDER (Ber., 1937, 70, [B], 251—257).—NEt₂ dissolves in liquid SO₂ to a brown solution from which on removal of SO₂ in presence of P₂O₅ colourless crystals of thionylidtriethylammonium sulphite (I), [(NEt₃)₂SO]SO₃, are formed. Addition of KBr to (I) in liquid SO₂ and removal of the excess of solvent in presence of P₂O₅ gives K₂S₂O₅ and thionylidtriethylammonium bromide (II) whereas in presence of KOH NH₄Et₃Br and SO₂ result. The formation of (II) is confirmed conductometrically. The evidence thus adduced supports the dissociation scheme, 2SO₂ \rightleftharpoons SO⁺⁺ + SO₃⁻⁻. Dry HCl is somewhat sol. in liquid SO₂ as shown by the enhanced conductivity, and treatment of (I) in the solvent with HCl gives NH₄Et₃Cl and SO₂. The reaction does not appear to be simple since HBr does not cause a similar change. Similarly NH₄Et₂ affords thionylid-diethylammonium sulphite, converted by KBr into thionylid-diethylammonium bromide and ultimately into the additive compound, [(NH₄Et₂)₂SO]Br₂·4KBr. Quinoline affords thionylid-

quinolinium sulphite, $[(C_9H_7N)_2SO]SO_3$, converted by KBr into the poorly-cryst. *thionylidiquinolinium bromide*. C_5H_5N appears to behave similarly. H. W.

Esters of sulphurous acid. IV. Action of sulphurous esters on amino-acids. W. VOSS and H. WULKAN (Ber., 1937, 70, [B], 388—392; cf. A., 1935, 79).—The action of Alk_2SO_3 on NH_2 -acids causes esterification and alkylation at N whereby Alk_2SO_3 is partly converted into $Alk \cdot SO_3Alk$ which is added to the *tert.* N. Glycine is transformed by Me_2SO_3 at 130° into *Me trimethylammoniumacetate methanesulphonate*, $SO_3Me \cdot NMe_3 \cdot CH_2 \cdot CO_2Me$, m.p. 117° after softening at 113° , also obtained from $NMe_2 \cdot CH_2 \cdot CO_2Me$ and $MeSO_3Me$ in EtOH; it is converted by boiling 20% HCl into MeCl and *trimethylammoniumacetic acid methanesulphonate* (I), m.p. 188° , also derived from $NMe_2 \cdot CH_2 \cdot CO_2H$ and $MeSO_3Me$ in H_2O , which does not react completely with $BaCO_3$ and is quantitatively decomposed by NaOH or $Ba(OH)_2$ into NMe_3 . *Pr^a dimethylaminoacetate*, b.p. $68-69^\circ/18$ mm. (*hydrochloride*, decomp. $60-70^\circ$; *methiodide*, m.p. $141-142^\circ$), cannot be obtained from $NH_2 \cdot CH_2 \cdot CO_2Pr^a$ and Me_2SO_3 but is derived from $CH_2Cl \cdot CO_2Pr^a$ and $NHMe_2$ in C_6H_6 at room temp. It is converted by $MeSO_3Me$ into the corresponding *N-methylmethane sulphonate*, m.p. $99-100^\circ$, which is hydrolysed to (I). *dl-Alanine* affords *Me trimethylammoniumpropionate methanesulphonate*, m.p. (indef.) $110-113^\circ$, hydrolysed to *trimethylammoniumpropionic acid methanesulphonate*, m.p. $152-153^\circ$. *l-Tyrosine* gives a non-cryst. *ester*, hydrolysed to *trimethyltyrosinebetaine methanesulphonate*, m.p. $175.5-176^\circ$. H. W.

Compounds producing hypoglycaemia. III. Synthesis of α -diguanydinomannitol hydrochloride. S. KAWAI and N. SUGIYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 31, 147—151).—*d*-Mannitol α -dichlorohydrin (Micheel, A., 1932, 834) and *o*- $C_6H_4(CO)_2NK$ at $135-140^\circ$ give the corresponding 1 : 6-*diphthalimido*-compound, decomp. $311-311.5^\circ$, hydrolysed by 5*N*-HCl at $165-175^\circ$ to the *dihydrochloride*, m.p. $136-137^\circ$, of the α -(NH_2)₂-derivative; this is condensed with $NH_2 \cdot C(OMe) \cdot NH_2 \cdot HCl \cdot NaOMe \cdot MeOH$ to give 1 : 6-*diguanydino-d-mannitol dihydrochloride*, decomp. 243° , $[\alpha]_D^{25} +14.4^\circ$ in H_2O (*flavianate*, decomp. $265-265.5^\circ$). J. W. B.

Determination of the configuration of natural α -amino-acids. P. PFEIFFER and W. CHRISTELEIT (Z. physiol. Chem., 1937, 245, 197—210; cf. Lifschitz, A., 1925, ii, 264).—The rotation dispersion exhibited by internal complex Cu and Ni salts (with asymmetric Cu and Ni atoms) of the NH_2 -acids from which proteins are built indicates that all these acids, no matter to which of the three configurative groups of Fischer *et al.* (A., 1908, i, 325) and Karrer *et al.* (A., 1931, 220) they belong, have the same configuration. It is suggested that NH_2 -acids having this configuration should be assigned to the *l*-type. The rotation dispersion curves of the Cu salts exhibit max. at the following λ : *l*(+)-alanine (I) 518, *l*(+)-valine 524, *l*(-)-leucine 535, *l*(+)-isoleucine (II), *l*(-)-phenylalanine (III) and *l*(-)-tyrosine (IV) about 522, Et *l*(-)-aspartate 520, *l*(-)-proline (V)

486 m μ . The curves of the following Cu salts exhibit min.: *d*(-)-valine at 516, *d*(+)-serine at 520, and (V) at 575 m μ . The max. and min. on the curve for the Ni salt of (I) are at 520 and 580 m μ , respectively. The Cu salt of *dl*-valine and the Ni salts of *dl*-alanine, (II), (III), and (IV) have been prepared. W. McC.

Colour reaction of glycine with ferric salts. II. J. V. DUBSKY and A. LANGER (Coll. Czech. Chem. Comm., 1937, 9, 1—11; cf. this vol., 9).—When $FeBr_3$ (1 mol.) and glycine (I) (1 mol.) in H_2O are evaporated at 50° the compound

$OH \cdot FeBr_2 \cdot FeBr_3 \cdot 2(I) \cdot H_2O$ is obtained. 1.5, 2, 2.5, 3, and 6 mols. of (I) similarly give the following compounds after trituration with EtOH:

$OH \cdot FeBr_2 \cdot FeBr_3 \cdot 3(I) \cdot H_2O$, softens at 177° , decomp. 181° , $OH \cdot FeBr_2 \cdot FeBr_3 \cdot 4(I) \cdot 3.5H_2O$, m.p. 112° (decomp.), $OH \cdot FeBr_2 \cdot 2(I) \cdot 2H_2O$, m.p. 125° (decomp. $>135^\circ$), $OH \cdot FeBr_2 \cdot FeBr_3 \cdot 6(I) \cdot 4H_2O$, m.p. 112° (decomp. $>130^\circ$), and $OH \cdot FeBr_2 \cdot FeBr_3 \cdot 6(I) \cdot 3H_2O$, m.p. 108° (decomp. $>125^\circ$). $Fe(NO_3)_3 \cdot 9H_2O$ (1 mol.) evaporated with (I) (1 mol.) in H_2O at 40° after extraction with $COMe_2$ affords the compound

$OH \cdot Fe(NO_3)_2 \cdot (I) \cdot H_2O$, m.p. 108° (decomp.); similarly with 1.5, 2, 3, 4, and 6 mols. of (I), mixtures are formed which after extraction with EtOH afford compounds $OH \cdot Fe(NO_3)_2 \cdot 2(I)$, m.p. 172° (decomp.), $OH \cdot Fe(NO_3)_2 \cdot 2(I) \cdot H_2O$, m.p. 183° (decomp.), $OH \cdot Fe(NO_3)_2 \cdot Fe(NO_3)_3 \cdot 5(I) \cdot 4H_2O$, swells at 145° , $OH \cdot Fe(NO_3)_2 \cdot Fe(NO_3)_3 \cdot 7(I) \cdot 4H_2O$, m.p. 90° (swells at 106°), and $OH \cdot Fe(NO_3)_2 \cdot 12(I)$, softens at 70° , m.p. 80° (decomp. after 122°), respectively, whilst $Fe_2(SO_4)_3$ with (I) (2 mols.) gives $3OH \cdot FeSO_4 \cdot 4(I) \cdot 15H_2O$, m.p. 125° (decomp.), and with (I) (4 mols.) yields $2OH \cdot FeSO_4 \cdot 5(I) \cdot 11H_2O$, m.p. 106° (decomp.). F. N. W.

***l*(+)- α -Aminobutyric acid as a constituent of proteins.** E. ABDERHALDEN and A. BAHN (Z. physiol. Chem., 1937, 245, 246—256).—Advantage is taken of the fact that halogenated fatty acids react at different rates with NMe_3 to separate mixtures of the corresponding NH_2 -acids. The Au salts of trimethylaminoacetic, *dl*- α -trimethylamino-propionic and *n*-butyric acid, obtained by the action of NMe_3 on the corresponding Br-compounds, have m.p. 208° , 240° , and 142° (decomp.), respectively. The isolation of *l*(+)- α -amino-*n*-butyric acid (I) from edestin and yeast by fractional crystallisation of acids and salts is described. The (I) fraction contains acids of the valine and leucine groups and the NMe_3 method cannot be applied because the rates of reaction do not differ sufficiently. Yeast protein yields also *l*(+)-alanine, *l*(+)-valine (*benzoate*, m.p. $118-119^\circ$), *l*(+)-norvaline, *l*(-)-leucine, *l*(+)-norleucine (*benzoate*, m.p. $127-128^\circ$), and *l*(+)-isoleucine and probably contains hydroxy-amino-acids. Formyl-*l*(+)-norleucine has m.p. $125-126^\circ$. W. McC.

Alkylation of β -aminocrotonic esters. W. M. LAUER and G. W. LONES (J. Amer. Chem. Soc., 1937, 59, 232—233).—Robinson's mechanism (J.C.S., 1916, 109, 1083) for the reaction between Et β -diethyl-aminocrotonate (I) and MeI is supported by the production of $CHAcEt \cdot CO_2Et$ (II) when Et β -methyl- and β -dimethyl-aminocrotonates and (I) are treated with EtI and the resultant salts hydrolysed (H_2O).

Et β -di-*n*-propylaminocrotonate, b.p. 149—151°/9 mm. (obtained by prolonged interaction of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and NHPr^2 at room temp.), and *Et*I give the salt, $[\text{NPr}^2\cdot\text{CMe}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}]^+\text{I}^-$, m.p. 114—116°, also hydrolysed (H_2O) to (II). H. B.

Optically active amino-acids. S. BERLINGOZZI and G. F. NALDI (Atti R. Accad. Lincei, 1936, [vi], 23, 874—878).—Methylaspartic acid in *N*-NaOH with PhSO_2Cl affords *benzenesulphonylmethylaspartic acid* (+ H_2O) (I), m.p. 195—197° (decomp.), the dibrucine salt of which, on fractional crystallisation and treatment with NaOH, yields the optical isomerides of (I) (with $2\text{H}_2\text{O}$), m.p. 190—191°, $[\alpha]_D^{20} \pm 9.7^\circ$ (Na salts in H_2O). The *l*-dibrucine salt, m.p. approx. 125° (decomp.), is more sol. than the *d*-dibrucine salt, m.p. approx. 130° (decomp.). F. O. H.

Reaction of creatinine with 1:3:5-trinitrobenzene, 2:4:6-trinitrotoluene, and 2:4:6-trinitrobenzoic acid. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1936, 70, 211—217).—Creatinine may be detected by colour reactions in alkaline solution with trinitro-benzene (pink-red), -toluene (brown-red), or -benzoic acid (red). The reaction is attributed to the formation of mol. complexes. J. D. R.

Correlation of configuration of norleucine to β -amino-hexane. P. A. LEVENE and S. MARDASHEW (J. Biol. Chem., 117, 707—711).—*d*-Norleucine, $[\alpha]_D^{20} -16.7^\circ$ in 20% HCl, gives (Bz_2S_2) *benzoyl-d-norleucine Et ester*, m.p. 76°, $[\alpha]_D^{20} +8.87^\circ$ in EtOH, which on reduction ($\text{Na} + \text{EtOH}$) yields *norleucinol hydrochloride*, $[\alpha]_D^{24} -0.95^\circ$ in H_2O , and this with HI followed by reduction (Raney's catalyst) yields β -amino-hexane hydrochloride, m.p. 102—103° (decomp.), and β -benzamido-hexane, m.p. 82°, $[\alpha]_D^{25} +0.8^\circ$ in EtOH, which rotates in the same direction as β -amino-hexane. A. LI.

Reaction between *d*-glutamic acid and ammonia or aniline. C. L. TSENG and (Miss) E. J. H. CHU (Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 4, 17—19).—Evaporation of glutamic acid (I) with aq. NH_3 causes decomp. of the NH_4 salt, but with NH_4Cl the hydrochloride of NH_4 H glutamate is formed. (I) does not react with NH_2Ph or $\text{NH}_2\text{Ph}\cdot\text{HCl}$. J. D. R.

***l*-Alanylsarcosylglycine and its carbobenzyloxy-derivative,** m.p. 108°. Hydrazides, m.p. 147—148° and 145—147°, of carbobenzyloxy-*d*- and -*l*-alanylglycine and benzyl esters, m.p. 116° and 114—116°, of carbobenzyloxy-*d*- and -*l*-alanylglycylglycine. Carbobenzyloxyglycyl-*dl*-proline, m.p. 129—130°, -*l*-alanine, m.p. 135°, and -*d*-alanine, m.p. 135°.—See A., III, 97.

Combination of cysteine with allylthiocarbimide. A. TODRICK and E. WALKER (Biochem. J., 1937, 31, 297—298; cf. A., 1926, 194).—Cysteine (I) with allylthiocarbimide gives α -N-allylthiocarb-amido- β -thiolpropionic acid, m.p. approx. 200° (decomp.). An analogous reaction occurs with cystine but not with (I) after blocking NH_2 with CH_2O . W. McC.

Colour reaction between nitroprusside and glutathione. G. SCAGLIARINI and G. AVONI (Atti

R. Accad. Lincei, 1936, [vi], 24, 215—218).—On the addition of a MeOH solution of KOH to a cold, conc. mixture of glutathione and Na nitroprusside in aq. MeOH an intense red coloration is obtained. This rapidly turns brown, and finally yellow $\text{K}_3[\text{Fe}(\text{CN})_6(\text{H}_2\text{O})]$ is pptd. The composition of the intermediate red product is indicated.

O. J. W.

Djengkolic acid, a new amino-acid containing sulphur. A. J. HIJMAN and A. G. VAN VEEN (Geneesk. Tijds. Nederl.-Ind., 1936, 76, 840—859; cf. A., 1935, 966).—Djengkolic acid (I), $\text{CH}_2[\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}]_2$, is present in the djengkol bean (*Pithecolobium lobatum*) (2%), which also contains 1 vitamin-B₁ unit per g., and in Sumatra "Boea Kabau" (*P. bubalinium*) (3—4%). It is similar to cystine in physiological action. Djengkol poisoning is due to separation of the acid in the urethra. A much simplified method of prep. for and biological tests with (I) are described. S. C.

Aliphatic dimethylamides. J. R. RUHOFF and E. E. REID (J. Amer. Chem. Soc., 1937, 59, 401—402).—The method previously described (A., 1931, 831) for the prep. of dimethylamides (I) from fatty acids (II) and NHMe_2 gives (except for HCO_2H) azeotropic mixtures [of (I) and (II)], which have b.p. slightly > those of (I). Acet-, b.p. 165°/758 mm., m.p. -20°, butyr-, b.p. 124.5°/100 mm., m.p. -40°, hept-, b.p. 172.5°/100 mm., m.p. -19°, and octo-dimethylamide, b.p. 187°/100 mm., m.p. -21°, are prepared by saturating the (II) with NHMe_2 at 35°, heating the product at 200°/5 hr. in a steel bomb, and removing H_2O and unchanged (II) with solid KOH. Propion-, b.p. 175.5°/765 mm., m.p. -45°, valer-, b.p. 141°/100 mm., m.p. -51°, and hexo-dimethylamide, b.p. 158°/100 mm., m.p. -42°, are prepared by addition of AlkCOCl to conc. aq. NHMe_2 at -20° to -10°. $\text{HCO}\cdot\text{NMe}_2$ has b.p. 153°/760 mm., m.p. -61°. Other physical data are given.

H. B.

Colorimetric determination of carbamide. J. A. SÁNCHEZ (Rev. Centr. Estud. Farm. Bioquim., 1935, 364—372; Chem. Zentr., 1936, i, 2399).— $\text{CO}(\text{NH}_2)_2$ is destroyed by HNO_2 , following de-proteinisation with Na_2WO_4 , and the excess of HNO_2 is determined colorimetrically by diazotising *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, and coupling with PhOH.

J. S. A.

Identification of nitriles. II. Additive compounds of nitriles with thiolacetic acid. F. E. CONDO, E. T. HINKEL, A. FASSERO, and R. L. SHRINER (J. Amer. Chem. Soc., 1937, 59, 230—232).— $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and RCN with dry HCl in absence or presence of Et_2O give the additive compounds, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CR}\cdot\text{NH}_2\cdot\text{HCl}$. The following are described: α -imino-ethyl-, decomp. 115°, -propyl-, decomp. 128°, -*n*-butyl-, decomp. 137°, -*n*-amyl-, decomp. 138°, -isoamyl-, decomp. 137°, -*n*-hexyl-, decomp. 136°, -isohexyl-, decomp. 128°, -*n*-heptyl-, decomp. 133°, -*n*-octyl-, decomp. 135°, -benzyl- (I), decomp. 125°, -*m*-, decomp. 169°, and -*p*-, decomp. 182°, -methylbenzyl-, and - β -phenylethyl-, decomp. 146°, -thiolacetic acid hydrochlorides. (I) is also prepared from $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ and $\text{NH}_2\cdot\text{CSPH}$ in Et_2O .

The decomp. temp. quoted are determined in a preheated bath and are corr. H. B.

Esters of phosphoric acid. III. Ethanolaminephosphoric acid and phosphorylcholine. R. H. A. PLIMMER and W. J. N. BURCH (Biochem. J., 1937, 31, 398—409).— POCl_3 (or $\text{H}_3\text{PO}_4 + \text{P}_2\text{O}_5$) with the appropriate base or NH_3 or NMe_3 with $\text{C}_2\text{H}_4\text{Cl}\cdot\text{H}_2\text{PO}_4$ [which with dil. alkalis readily affords $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{H}_2\text{PO}_4$] yield ethanolaminephosphoric acid (cf. Outhouse, A., 1936, 230), m.p. 232—233° (decomp.) [*Ba* ($3\text{H}_2\text{O}$), *Ba H* ($5\text{H}_2\text{O}$), and NH_4 ($2\frac{1}{2}\text{H}_2\text{O}$) salts], and phosphorylcholine (anhydride) [*Ca* ($4\text{H}_2\text{O}$) and *Ba* ($4\text{H}_2\text{O}$) salts]. The esters are hydrolysed by *N*-HCl and bone-, kidney-, and intestine-phosphatase but are stable to *N*-NaOH at 100°. F. O. H.

Preparation and analysis of silicon tetraethyl and tetrabutyl. C. L. TSENG and T. Y. CHAO (Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 4, 21—37).— MgBu^nBr and SiCl_4 in Et_2O afford *Si tetra-n-butyl*, b.p. 150—153°/17 mm. Analysis of org. Si compounds is carried out by fusion with Na_2O_2 in a Parr bomb, followed by determination of SiO_2 . J. D. R.

Uninuclear tripropylenediaminechromic ion, binuclear tripropylenediaminecobaltic ion, and their sulphato-, oxalato-, phosphato-, and arsenato-complexes.—See A., I, 184.

Dehydration of dimethylcyclobutylcarbinol. B. A. KAZANSKI (J. Gen. Chem. Russ., 1936, 6, 1598—1601).— CS_2 is added to a solution of the K salt of dimethylcyclobutylcarbinol in decahydronaphthalene, and the xanthate so formed is treated with MeI at 100°. The mixture of isomeric isopropenylcyclobutanes, b.p. 98—100°, so obtained yields isopropylcyclobutane, b.p. 90.5—91.5°, when hydrogenated. R. T.

Halogen migration under the influence of aluminium chloride. III. C. D. NENITZESCU and D. CURCĂNEANU (Ber., 1937, 70, [B], 346—348; cf. this vol., 58).—The repulsive effect of halogen is marked but not so pronounced as that of :CO or $\cdot\text{Oalk}$ since the repelled atom does not entirely seek the most distant available position in the mol. Gradual addition of 1:2-dibromocyclohexane to AlCl_3 in C_6H_6 at 50° yields 1:4-diphenylcyclohexane, m.p. 170°, dehydrogenated by Se at 320—350° to *p*- $\text{C}_6\text{H}_4\text{Ph}_2$, and smaller amounts of cyclohexylbenzene (dehydrogenated to Ph_2) and 1:3-diphenylcyclohexane, b.p. 196—198°/17 mm., dehydrogenated to *m*- $\text{C}_6\text{H}_4\text{Ph}_2$, m.p. 87°. 1:2-Dichlorocyclohexane behaves similarly. 1:2-Diphenylcyclohexane does not appear to be formed. 2-cyclohexylcyclohexanone is converted by MgPhBr into 1-phenyl-2-cyclohexylcyclohexanol, b.p. 208—212°/26 mm., m.p. 70—72°, transformed by Se at about 330° into triphenylene, m.p. 196—197°. H. W.

Colorimetric determination of carotene.—See A., III, 162.

Reactivity of the substituents in benzene derivatives. A. MANGINI (Mem. R. Accad. Italia, 1936, 7, 1—23; cf. A., 1936, 975).—Fry's polarity rule is criticised. The use of dipole moment data in predicting the reactivity of groups in tri-substituted

derivatives of C_6H_6 (containing Cl, NO_2 , and Me) is discussed. O. J. W.

Dipole moment, configuration, and reactivity of aromatic nitro-derivatives. A. MANGINI (Mem. R. Accad. Italia, 1936, 7, 241—276; cf. preceding abstract).—A further discussion of the use of dipole moments in determining the reactivity of the substituents in trihalogeno- and $(\text{NO}_2)_3$ -derivatives of C_6H_6 , and also in tetra- and penta-substituted C_6H_6 . O. J. W.

Bromination of halogenobenzenes in the gaseous phase: influence of temperature and catalysts on the substitution type. J. P. WIBAUT and M. VAN LOON (Nature, 1937, 139, 151; cf. A., 1933, 942).—Data for the monobromination of PhBr, PhCl, and PhF in the gaseous phase between 380° and 500°, in presence of artificial graphite as contact agent, are recorded. Below 400° this bromination belongs to Holleman's *o-p* type, and above 450°, to the *m* type; this disagrees with current theories on C_6H_6 substitution. With FeBr_3 as catalyst different results are obtained. Between 200° and 450° there is only a gradual change in the relative amounts of isomerides and no change of substitution type. L. S. T.

Organic and inorganic chemistry of iodine oxides. I. MASSON (Nature, 1937, 139, 150—151).—In H_2SO_4 media of hydration $< \text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{HIO}_3$ and PhCl give an 80% yield of the *p*-iodonium derivative; C_6H_6 yields diphenyliodonium salts, and its derivatives with *o-p*-directing substituents which are not too highly activating react in the same way; *m*-directing substituents such as NO_2 prevent the reaction. With $\text{I}_2\text{O}_3, \text{SO}_3, \frac{1}{2}\text{H}_2\text{O}$ instead of HIO_3 , the yield of iodonium salts from PhCl becomes quant. I_2O_3 easily effects two new aromatic substitutions; with C_6H_6 and its *o-p*-directing derivatives *p*-iodonium salts are formed, whilst with PhNO_2 or PhSO_3H direct introduction of IO is obtained with *m*-orientation.

The reaction $2\text{I}_2 + 3\text{I}_2\text{O}_5 \rightleftharpoons 5\text{I}_2\text{O}_3$ is displaced \leftarrow by heat and completely by H_2O , and \rightarrow by an acid strong enough to convert I_2O_3 into a salt. The sulphate is quantitatively obtained from 2I_2 and $3\text{I}_2\text{O}_5$ by shaking with cold conc. H_2SO_4 . The thermal dissociation $\text{I}_2\text{O}_5 \rightarrow \text{O}_2 + \text{I}_2\text{O}_3 \rightarrow \text{I}_2 + 2\frac{1}{2}\text{O}_2$ can be exactly arrested at the middle stage by heating I_2O_5 in fuming instead of conc. H_2SO_4 , which stabilises tervalent cationic iodine as a sol. sulphate even at 220°. Fuming H_2SO_4 also oxidises I in the cold, forming manganate-green or deep blue solutions, and liberating SO_2 . IO_2 and I_4O_9 are probably iodosous iodates, $\text{I}_2\text{O}_3, n\text{I}_2\text{O}_5$. L. S. T.

[Benzene- and *p*-toluene-]sulphonic acid esters. G. E. HAZLET (J. Amer. Chem. Soc., 1937, 59, 287).—*o*-, *m*-, and *p*-Bromophenyl benzenesulphonates, m.p. 54—56°, b.p. 217—218°/10.5 mm., and m.p. 50—55°, respectively, and *p*-toluenesulphonates, m.p. 77—79°, 52—54°, and 93—95°, respectively, and *o*-, *m*-, and *p*-diphenyl benzenesulphonates, m.p. 66—68°, b.p. 273°/16 mm., and m.p. 104—105°, respectively, and *p*-toluenesulphonates, m.p. 64—66°, 52—54°, and 178.5—179.5° (lit. 177°), respectively, are prepared ($\text{C}_5\text{H}_5\text{N}$ method). H. B.

Action of sulphinates on 1:5-dichloro-2:4-dinitrobenzene. A. LIVINGSTONE and J. D. LONDON

(J.C.S., 1937, 246—249).— p - C_6H_4Me -SNa and 1:5:2:4- $C_6H_2Cl_2(NO_2)_2$ (I) in EtOH afford 2:4-dinitro-1:5-di- p -tolylthiobenzene (II), m.p. 233°, and 5-chloro-2:4-dinitro-4'-methylthiobenzene (III), m.p. 147—148°. Similarly, PhSNa affords 2:4-dinitro-1:5-diphenylthiobenzene, m.p. 253°, and 5-chloro-2:4-dinitrodiphenyl sulphide (IV), m.p. 108°. (II) when oxidised (H_2O_2 -AcOH) affords 2:4-dinitro-1:5-di- p -tolylsulphonylbenzene (V), m.p. 228° [also formed from (I) and p - C_6H_4Me -SO₂H in EtOH], which with C_6H_4Me -SNa in EtOH regenerates (II). Similar methods yield 2:4-dinitro-1:5-diphenylsulphonylbenzene (VI), m.p. 251°. p - C_6H_4Me -SO₂Na with (I) in EtOH- H_2O , or (V) in AcOH, affords 1:2:4:5-tetra- p -tolylsulphonylbenzene (VII), m.p. 315°, whilst (VI) and PhSO₂Na in AcOH-(CH₂·OH)₂ yield 1:2:4:5-tetraphenylsulphonylbenzene, m.p. 305°. (V) or (VII) with MeOH-NH₃ gives 2:4-diamino-1:5-di- p -tolylsulphonylbenzene, m.p. 293°, also obtained by reduction (SnCl₂) of (V). With boiling piperidine, (V) and (VII) give 2:4-dipiperidino-1:5-di- p -tolyl, m.p. 228°, and (VI) 2:4-dipiperidino-1:5-diphenylsulphonylbenzene, m.p. 221°. (III) is oxidised (AcOH- H_2O_2) to 5-chloro-2:4-dinitro-4'-methylthiobenzene (VIII), m.p. 198°, converted by p - C_6H_4Me -SNa in EtOH-dioxan into a mixture of (II) and (III). Similarly, (IV) is oxidised to 5-chloro-2:4-dinitrodiphenylsulphide, m.p. 187°. 5-Chloro-2:4-dinitropiperidinobenzene (IX) with p - C_6H_4Me -SO₂Na in EtOH yields 2:4-dinitro-5-piperidino-4'-methylthiobenzene (X), m.p. 180°, also obtained from (VIII) with excess of $C_5H_{11}N$, whilst the corresponding sulphide (XI), m.p. 192°, is obtained from (III) with piperidine, or from (X) or (IX) with p - C_6H_4Me -SNa in EtOH. With p - C_6H_4Me -SO₂H in AcOH (VIII) affords (V), but (III) and (IX) are unchanged. There appears therefore to be no fundamental difference in the mobilities of the two Cl atoms in (I). J. D. R.

Mobility of groups in certain nitrodiphenylsulphones. J. D. LOUDON and T. D. ROBSON (J.C.S., 1937, 242—246).—4:3:1- $C_6H_3Cl(NO_2)_2$ -SO₂Cl, with PhCl and AlCl₃ yields 4:4'-dichloro-3-nitrodiphenylsulphide (I), m.p. 130° [also produced by nitration (H_2SO_4 -KNO₃) of 4:4'-dichlorodiphenylsulphide], converted by piperidine into 4'-chloro-3-nitro-4-piperidinodiphenylsulphide, m.p. 80°. (I) with p - C_6H_4Cl -SO₂Na (II) in EtOH affords 1-nitro-2:5-di- p -chlorobenzenesulphonylbenzene, m.p. 231°, also prepared from (II) and 4'-chloro-2:4-dinitrodiphenylsulphide in boiling (CH₂·OH)₂. 2:5:1- $C_6H_3Cl_2$ -NO₂ (III) with p - C_6H_4Me -SH in EtOH affords 4-chloro-2-nitro-4'-methylthiobenzene (IV), m.p. 121°, oxidised (H_2O_2 -AcOH) to the sulphone (V), m.p. 124°. (III) and p - C_6H_4Me -SO₂Na in EtOH yield (IV) and 1-nitro-2:5-di- p -tolylsulphonylbenzene, also prepared from (IV) and p - C_6H_4Me -SO₂Na in boiling (CH₂·OH)₂. 2-Chloro-4-nitro-4'-methylthiobenzene (VI), m.p. 122°, and -sulphone (V), m.p. 125°, are prepared by the methods described above for their isomerides. With piperidine, (IV) yields 2-nitro-4-piperidino-, m.p. 183°, and 4-chloro-2-piperidino-, m.p. 121°, -4'-methylthiobenzene, whilst (V) affords 4-nitro-2-piperidino-4'-methylthiobenzene, m.p.

171°. 2-Chloro-4-amino-, m.p. 165°, and 4-chloro-2-amino-, m.p. 136°, -4'-methylthiobenzene are obtained by reduction (SnCl₂) of (V) and (IV), respectively, the latter also being formed from (IV) and MeOH-NH₃. (IV) and (V) with NaOMe yield 4-chloro-2-methoxy-, m.p. 117°, and 2-chloro-4-methoxy-, m.p. 118°, -4'-methylthiobenzene, respectively, the latter also being the product from (V) and MeOH-NH₃. 2-Amino-4'-methylthiobenzene by the Sandmeyer reaction yields 2-chloro-4'-methylthiobenzene, m.p. 113°. 2- (VI), m.p. 118°, and 4-, m.p. 134°, -piperidino-4'-methylthiobenzene are prepared from the corresponding chlorosulphones and a mixture of (VI) and 2-nitropiperidinobenzene. 1:4:3- $C_6H_3MeClNO_2$ is obtained from 2-nitro-4-methylthiobenzene and p - C_6H_4Me -SH in NaOH afford 2-nitrodi- p -tolyl sulphide, m.p. 116°, oxidised (H_2O_2 -AcOH) to the sulphone, m.p. 132° which with piperidine yields 2-piperidinodi- p -tolylsulphide, m.p. 148°. J. D. R.

Catalytic polymerisation of ethylenic derivatives. O. SCHMITZ-DUMONT, K. THÖMKE, and H. DIEBOLD (Ber., 1937, 70, [B], 175—182).—The tendency towards polymerisation of an ethylenic compound CR_2CH_2 increases with increasing polarity of the ethylenic linking up to a certain point, beyond which it is diminished or nullified. p - C_6H_4Me -CPh:CH₂ is slowly converted by AcOH- H_2SO_4 (4:1) at room temp. into the dimeride (?), $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di- p -tolyl- Δ^a -butene, m.p. 113—114°. Under similar conditions (p - C_6H_4Me)₂C:CH₂ affords $\alpha\alpha\gamma\gamma$ -di- p -tolyl- Δ^a -butene (I), m.p. 107.5—108°, smoothly depolymerised by conc. H_2SO_4 , so that polymerisation by acid appears to lead to an equilibrium dependent on the concn. of the acid. (I) is gradually converted by Br (4 mols.) in CHCl₃ into HBr and $\beta\beta$ -dibromo- $\alpha\alpha$ -di- p -tolylethylene (II), m.p. 119.5—120°, and by 1 mol. of Br into the compound, $C_{32}H_{30}$, m.p. 247—248°, which is not an intermediate in the production of (II) since it is transformed by Br (4 mols.) into the substance, $C_{32}H_{28}Br_2$, m.p. 172—173°. p -OMe- C_6H_4 -CPh:CH₂ gives the dimeride, $C_{30}H_{28}I_2$, m.p. 112—114°, depolymerised by conc. H_2SO_4 at 25°, and converted by Br (4 mols.) into $\beta\beta$ -dibromo- α -phenyl- α - p -anisylethylene (III), m.p. 111—113° (from EtOH) or m.p. 113.5° (from AcOH), and by Br (1.25 mols.) into the compound, $C_{30}H_{26}O_2$, m.p. 222.5—223.5°, reduced by Na in boiling amyl alcohol to a compound, m.p. 119.5—120°. Oxidation of (III) by CrO₃ in AcOH containing KHSO₄ gives p - C_6H_4 Bz-OMe. Dibromoanisyl ketone is transformed by MgMeBr in C_6H_6 into $\alpha\alpha$ -di-3-bromo-4-methoxyphenylethylene, m.p. 111.5°, slowly converted by H_2SO_4 -AcOH into the dimeride, $C_{32}H_{28}O_4Br_4$, m.p. 179—179.5°, which with Br (4 mols.) affords $\beta\beta$ -dibromo- $\alpha\alpha$ -dibromoanisylethylene, m.p. 150°, and with Br (1 mol.) gives the substance, $C_{32}H_{26}O_4Br_4$, m.p. 178—179°. Di- p -anisylethylene is not polymerised by H_2SO_4 -AcOH.

H. W.

Orientation effects in the diphenyl series. XIII. Nitration of four 2-halogeno-4:4'-dimethylthiobenzene. E. E. J. MARLER and E. E. TURNER (J.C.S., 1937, 266—271).—2-Amino-4:4'-

dimethyldiphenyl is converted via the diazonium borofluoride into 2-fluoro- (I), m.p. 73–74°, and by the Sandmeyer reaction into 2-chloro- (II), m.p. 32–33°, 2-bromo- (III), b.p. 183–187°/12 mm., and 2-iodo- (IV), b.p. 200–205°/15 mm., -4:4'-dimethyldiphenyl. (I) is nitrated (HNO_3 -AcOH) to 2-fluoro-2'-nitro-, m.p. 89–90°, which is reduced (SnCl_2) to 2-fluoro-2'-amino-, m.p. 105–106°, converted by the Sandmeyer reaction into 2:2'-difluoro-4:4'-dimethyldiphenyl, m.p. 97–98°. (II) is nitrated (HNO_3 -AcOH) and reduced (SnCl_2) to a mixture (2:6:1) of 2-chloro-2'-amino- (V) (Ac derivative, m.p. 115–116°) and 2-chloro-?-amino-, m.p. 75–77°, -4:4'-dimethyldiphenyl [Ac derivative, m.p. 123–124°; hydrochloride, m.p. 223–224° (decomp.)]. (III) by nitration and reduction affords a mixture (1:8:1) of 2-bromo-2'-amino- (VI) (Ac derivative, m.p. 134–135°) and 2-bromo-?-amino- (Ac derivative, m.p. 146–147°; hydrochloride, m.p. 227–229°) -4:4'-dimethyldiphenyl. Similarly, (IV) yields a mixture (2:3:1) of 2-iodo-2'-amino- (VII) (Ac derivative, m.p. 160–161°) and 2-iodo-?-amino- (Ac derivative, m.p. 165–166°; hydrochloride, m.p. 222–224° (decomp.)) -4:4'-dimethyldiphenyl. (V), (VI), and (VII) by the Sandmeyer reaction yield, respectively, 2:2'-dichloro-, m.p. 90°, 2:2'-dibromo-, m.p. 114–115°, and 2:2'-di-iodo-, m.p. 116–117°, -4:4'-dimethyldiphenyl. In the conversion of 2-NH₂- into 2-halogeno-compounds 2-hydroxy-4:4'-dimethyldiphenyl, m.p. 57–58° (p-toluenesulphonate, m.p. 130°), is formed. J. D. R.

Action of selenium on compounds containing quaternary carbon atoms. G. R. CLEMO and H. G. DICKENSON (J.C.S., 1937, 255–257).— α -Dimethylsuccinic anhydride and C_6H_6 with AlCl_3 afford β -benzoyl- α -dimethylpropionic acid, (I), m.p. 173° (transformed by N_2H_4 into 6-keto-3-phenyl-5:5-dimethyltetrahydropyridazine, m.p. 167–168°), reduced (Zn-HCl) to δ -phenyl- α -dimethylbutyric acid, b.p. 140–150°/0.2 mm., m.p. 97°, which with 80% H_2SO_4 affords 1-keto-2:2-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. 137°/15 mm., reduced (Zn-HCl) to 2:2-dimethyl-1:2:3:4-tetrahydronaphthalene (II), b.p. 104°/12 mm. α -Methyl- α -ethylsuccinic anhydride, C_6H_6 , and AlCl_3 give β -benzoyl- α -methyl- α -ethylpropionic acid, m.p. 94–95° (pyridazine, m.p. 108°), reduced (Zn-HCl) to γ -phenyl- α -methyl- α -ethylbutyric acid, m.p. 63°, which with 70% H_2SO_4 affords 1-keto-2-methyl-2-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 140°/13 mm., reduced to 2-methyl-2-ethyl-1:2:3:4-tetrahydronaphthalene (III), b.p. 118°/20 mm. (II) and (III) could not be dehydrogenated by long heating with Se at 280–360°.

J. D. R.

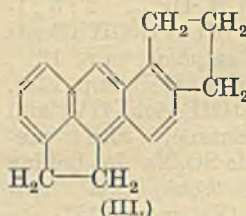
Structure of some derivatives of fluorene and fluorenone. E. D. HUGHES, (MRS.) C. G. LE FÈVRE, and R. J. W. LE FÈVRE (J.C.S., 1937, 202–207).—Dipole moments of fluorene, 2:7- and 2:5-dinitro- and 2:7-dibromo-fluorene, fluorenone, 2-nitro-, 2:7- and 2:5-dinitro-, and 2:7-dibromo-fluorenone are recorded and discussed in relation to possible stereochemical structures. J. D. R.

Influence of solvent on the course of chemical reactions. XII. Heat of dissolution and energy

of activation in the sulphonation of anthraquinone. K. LAUER and R. ODA (Ber., 1937, 70, [B], 333–345).—The energies of activation, determined experimentally and changing with certain regularities, of the sulphonation of anthraquinone (I) by H_2SO_4 of varying concn. can be reduced to an energy of activation const. for all conditions by taking into account the heat of dissolution of (I) and those of the required amounts of H_2O or SO_3 in H_2SO_4 , H_2O . It is possible by calculation to eliminate the influence of the solvent on the participants in the change and to apply the determined energies of activation to reaction in the gas phase. The energy of activation thus deduced is const. for all concns. of aq. and fuming H_2SO_4 . H. W.

Perylene and its derivatives. XLIX. Perylene trihalides of K. Brass and E. Clar. A. ZINKE and A. PONGRATZ [with K. SCHOLTIS and F. HANUS] (Ber., 1937, 70, [B], 214–218; cf. A., 1936, 1102).—Contrary to Brass and Clar (A., 1932, 57; 1936, 1241), the immediate product of the action of Br on perylene (I) contains 4Br. When exposed to a current of air adherent Br is rapidly removed and a tetrabromide results which then slowly loses HBr, giving a mixture of substances from which 3:9-dibromoperylene (II) is isolated by crystallisation from org. media. (II) absorbs Br vapour giving a product of varying composition whereas 3:9-dichloroperylene is unaffected. (I) is transformed by I in C_6H_6 into cryst. products the I content of which depends on the concn. and total amount of I and is invariably > that required for a tri-iodide. Crystallisation of the products from C_6H_6 containing I yields materials in which the I content is frequently > that required for a tetraiodide. H. W.

Aceanthrene derivatives related to cholanthrene. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1937, 59, 394–398).—4-Chlorohydrindene (I), b.p. 108–110°/24 mm., prepared by Clemmensen reduction of the α -hydrindone, m.p. 90–90.5° (from $o\text{-C}_6\text{H}_4\text{Cl-CH}_2\text{-CH}_2\text{-COCl}$ and AlCl_3 in CS_2), with CuCN and $\text{C}_5\text{H}_5\text{N}$ at 220° gives 4-cyanohydrindene (II), b.p. 139–141°/22 mm., hydrolysed (conc. HCl at 180–200°) to hydrindene-4-carboxylic acid, m.p. 152.5–153.5° [amide, m.p. 173–173.5°, also obtained during the prep. of (II)]. Li 4-hydrindyl [from (I) and Li in Et_2O and N_2] and (II) at –70° to room temp. afford di-4-hydrindyl ketone, b.p. 206–209°/4 mm., m.p. 77–78°, which when heated at 415–420°/30 min. gives 21% of 1:2-cyclopenteno-5:10-acanthrene (III),



m.p. 175.5–176° (picrate, m.p. 104.5–141.5°). (III) is oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$, AcOH) to 1:2-cyclopenteno-9:10-anthraquinone-5-acetic acid, m.p. 284–285° (decomp.), attempted decarboxylation (CuCO_3 in quinoline) of which gives a little of an impure neutral quinone, m.p. 121–123°. The Grignard reagent from 3-bromo-*o*-xylene (prep. described; cf. Stallard, J.C.S., 1906, 89, 808) and (II) afford 4-2':3'-dimethylbenzoylhydrindene, b.p. 183–186°/4 mm., m.p. 75–75.5°, which when heated at 420–430°/2 hr.

gives small amounts of 1 : 2-dimethyl-5 : 10-aceanthrene (IV), m.p. 206—207° (picrate, m.p. 169—170°), and 1-methyl-5 : 6-cyclopentenoanthracene, m.p. 131—132° (picrate, m.p. 156—157°; corresponding quinone, m.p. 125—127°). All m.p. are corr. (III) and (IV) have been synthesised for comparison with cholanthrene [1 : 2-benz-5 : 10-aceanthrene] (V). 10-Methyl- and 5 : 10-dimethyl-1 : 2-benzanthracene (this vol., 93) have the same order of carcinogenic activity as (V) and methylcholanthrene. H. B.

Optical activity dependent on restricted rotation in a benzene derivative. W. H. MILLS and R. M. KELHAM (J.C.S., 1937, 274—278).—The Na derivative of p -C₆H₄Me·NHAc with Me₂SO₄ in C₆H₆ gives its *N*-Me derivative, converted by conc. H₂SO₄—NH₄VO₃ at 170—180° into Na *N*-methyl-*p*-toluidine-3-sulphonate, which with Ac₂O affords Na *N*-acetyl-*N*-methyl-*p*-toluidine-3-sulphonate (I), +2H₂O, m.p. 81—82°, and anhyd., m.p. 277—279° (decomp.). The overlap of the two *o*-groups causes mol. dissymmetry and resolution of (I) is effected by crystallisation of the *brucine* salt, +2H₂O and anhyd., which exhibits mutarotation (half-change, 169 min.). From this is obtained d-*Na N*-acetyl-*N*-methyl-*p*-toluidine-3-sulphonate, initial $[\alpha]_{461}^{20} +6.06^\circ$ in H₂O. Determinations of the rate of racemisation at 16.6°, 24°, 28°, and 35° show that the unimol. velocity coeffs. are represented by the relationship $k = 2.797 \times 10^{14} \cdot e^{-22.613/RT}$. J. W. B.

Action of benzylamine on aliphatic esters. C. A. BUEHLER and C. A. MACKENZIE (J. Amer. Chem. Soc., 1937, 59, 421—422).—Form-, m.p. 59.8—60.4° (lit. 49°), acetyl-, m.p. 60.7—61.3°, propion-, m.p. 42.6—43.7°, *n*-butyl-, m.p. 36.9—38°, isobutyl-, m.p. 87—88°, *n*-valeryl-, m.p. 41.1—41.8°, *n*-hexyl-, m.p. 50.3—51.4°, and croton-, m.p. 112.5—113.6°, -benzylamides are prepared from the appropriate AlkCO₂Et and CH₂Ph·NH₂ (I) in boiling aq. EtOH or aq. dioxan. Mono-, m.p. 93—93.6°, di-, m.p. 94.8—95.6°, and tri-, m.p. 93.6—94.4° (lit. 90—91°), -chloroacetbenzylamides are obtained from the respective Et esters and (I) in H₂O at about 0°. CH₂Ph·NH₂·HCl, m.p. 263.3—265.7° (lit. 255.5—258°), and CH₂Ph·NH₂·HBr, m.p. 223—224.1° (lit. 215—216°), are obtained when (I) (2 mols.) is heated with CHCl₃·CO₂Et (R = H, Me) and CHBr₃·CO₂Et (R = H, Et), respectively. All m.p. are corr. H. B.

Reactions of α -naphthylhydroxylamine with sulphuric or hydrochloric acid. J. PAJAK (Rocz. Chem., 1936, 16, 551—559).—The chief product obtained by boiling α -C₁₀H₇·NH·OH with 10—30% H₂SO₄ is 1 : 4-C₁₀H₆(OH)₂, together with 1 : 4-OH·C₁₀H₆·NH₂, whilst with HCl in aq. EtOH the sole product isolated was 4 : 1-C₁₀H₆Cl·NH₂ (Ac₂ derivative, m.p. 135°). R. T.

Carbamide derivatives and their absorption by cellulose. K. BRASS, F. OPPELT, and A. WEICHERT (J. pr. Chem., 1937, [ii], 148, 35—52).—Passage of CS₂ into p -NH₂·C₆H₄·SO₃H (I)-aq. Na₂CO₃ gives the Na₂ salt (II) of *s*-di-*p*-sulphophenylthiocarbamide; p -NH₂·C₆H₄·SO₃Na with CS₂—3% H₂O₂ in aq. EtOH gives the Na₂ salt (III) of *s*-di-*p*-sulphophenylthiocarbamide (Ca salt), whilst prolonged treatment (4

weeks) similarly converts 1 : 4-NH₂·C₁₀H₆·SO₃H (IV) into the Na₂ salt (V) of *s*-di-4-sulphonaphthylthiocarbamide. By lit. methods are prepared the Na salts of *s*-di- α - and *s*-di- β -naphthylthiocarbamide, *s*-di-4-sulpho- α -naphthyl- (VI) (phenylhydrazone + H₂O and anhyd. of the free acid), *s*-di-(8-hydroxy-6-sulpho- β -naphthyl)- (VII), and *s*-di-(5-hydroxy-7-sulpho- β -naphthyl)- (VIII)-carbamide. The absorption of the Na salt of J-acid and of γ -acid [2 : 5 : 7- and 2 : 8 : 6-NH₂·C₁₀H₅(OH)·SO₃H] by viscose artificial silk fibres approaches equilibrium with the solution (partition coeff. 0.795 and 0.758, respectively), 1.90 and 2.01%, respectively, of the fibre-wt. being absorbed. Absorption of the corresponding carbamido-derivatives (VIII) and (VII) under the same conditions amounts to 5.26 and 5.20%, respectively. The simpler SO₃H-acids (I) and (IV) and their derivatives (II), (III), (V), and (VI) are not absorbed by the fibre: hence no single hypothesis will explain the substantivity. J. W. B.

Diphenyl series. VIII. Bromination of 2-nitro-4'-amino- and 4'-nitro-2-amino-diphenyl. V. BELLAVITA (Atti Congr. naz. Chim., 1935, 5, 12 pp.; Chem. Zentr., 1936, i, 2341—2342).—Br in AcOH with 2-nitro-4'-aminodiphenyl yields 4 : 5-dibromo-2-nitro-4'-aminodiphenyl (I), m.p. 141° (Ac derivative, m.p. 182—183°), reduced (Sn—HCl) to 4 : 5-dibromo-2 : 4'-diaminodiphenyl (II), m.p. 108—109° (Ac₂ derivative, m.p. 245°), which is converted by diazotisation and reduction with H₃PO₂ into 3 : 4-dibromodiphenyl, m.p. 42°. (I), similarly, affords 4 : 5-dibromo-2-nitro-, m.p. 108°, and (Sn—HCl) -2-amino-diphenyl, m.p. 86° [hydrochloride, m.p. 215° (decomp.); Ac derivative, m.p. 151—152°], which is converted (Sandmeyer) into 2 : 4 : 5-tribromodiphenyl, m.p. 68°. (I), by the Sandmeyer reaction, yields 4 : 5 : 4'-tribromo-2-nitrodiphenyl, m.p. 144°, reduced to 4 : 5 : 4'-tribromo-2-aminodiphenyl (III), m.p. 113° (Ac derivative, m.p. 189—190°). (II), by the Sandmeyer reaction, yields 2 : 4 : 5 : 4'-tetrabromodiphenyl, m.p. 135°, also obtained from (III). Diazotisation of (III) followed by H₃PO₂ reduction yields 4 : 5 : 4'-tribromodiphenyl (IV), m.p. 102°. Br in AcOH with 4'-nitro-2-aminodiphenyl yields 3 : 4-dibromo-4'-nitro-2-aminodiphenyl (V), m.p. 189° (Ac derivative, m.p. 158°), reduced (Sn—HCl) to 3 : 4-dibromo-2 : 4'-diaminodiphenyl (VI), m.p. 105° (Ac₂ derivative, m.p. 180°). Reduction of the diazo-solution of (V) yields 3 : 4-dibromo-4'-nitrodiphenyl, m.p. 160°, reduced (Sn—HCl) to 3 : 4-dibromo-4'-aminodiphenyl, m.p. 114° (hydrochloride; Ac derivative, m.p. 217—218°), converted (Sandmeyer) into (IV). (V) by the Sandmeyer reaction yields 2 : 3 : 4-tribromo-4'-nitrodiphenyl, m.p. 148°, reduced (Sn—HCl) to 2 : 3 : 4-tribromo-4'-aminodiphenyl (VII), m.p. 116° (hydrochloride; Ac derivative, m.p. 220°), which by diazotisation and H₃PO₂ reduction yields 2 : 3 : 4-tribromodiphenyl, m.p. 225—227°. (VI), by the Sandmeyer reaction, yields 2 : 3 : 4 : 4'-tetrabromodiphenyl, m.p. 127°, also obtained from (VII). No Br₂-compound is produced in the reactions yielding (I) and (V), the structure of which has been established by interaction with piperidine. H. N. R.

Synthesis of 1-aminophenanthrene. W. E. BACHMANN (J. Amer. Chem. Soc., 1937, 59, 420—

421).—The oxime of 1-keto-1:2:3:4-tetrahydrophenanthrene is reduced (Na-Hg, EtOH-AcOH) to 1-amino-1:2:3:4-tetrahydrophenanthrene, the Ac derivative, m.p. 176°, of which is dehydrogenated (Pt-black at 320°; S at 250–260°) to the Ac derivative of 1-aminophenanthrene. H. B.

Manufacture of 3:6-dihalogeno-2:4-dinitroanilines.—See B., 1937, 119.

Manufacture of 3:4'-dinitro-4-amino-6-methyldiphenylamine.—See B., 1937, 119.

Esters of N-p-aminoarylcabamic acids.—See B., 1937, 120.

Sugar derivatives of 4:5-diamino-o-xylene.—See B., 1937, 120.

Azo-dyes and immunobiology. Schultz-Dale experiments with bis-*p*-succinanic acid-azoresorcinol. H. E. FIERZ-DAVID, W. JADASSOHN, and W. F. ZÜRCHER (Helv. Chim. Acta, 1937, 20, 16–37).—Revised methods are given for the prep. of succin-*p*-nitroanilic acid, m.p. 196–197° (corr.), succin-*p*-aminoanilic acid, m.p. 183° (corr.), *p*-succinanic acid-azoresorcinol (I), bis-*p*-succinanic acid-azoresorcinol (II), and *p*-succinanic acid-azoprotein (III) and materials obtained according to Landsteiner *et al.* (A., 1933, 82) are also used. In the Schultz-Dale experiment guinea-pigs pre-injected with (III) (horse serum) are sensitised to anaphylactic shock from injection of (III) (hen serum) but not from injection of (II). Guinea-pigs treated with (II) prep. according to Landsteiner are sensitive to (III) in the Schultz-Dale experiment but not to (II). It is shown that (II) *in vitro* can undergo re-coupling with alkaline R salt solution. (II) obtained according to Landsteiner is sol. in much conc. alkali to a violet solution whereas that obtained by the author's method remains orange-red when treated similarly; the products differ in their behaviour towards R salt *in vitro*. Guinea-pigs are seldom sensitised to (III) by pre-treatment with technical (II). It thus appears that Landsteiner's (II) undergoes re-coupling with (III) *in vivo*. The observed physiological action of (II) does not therefore depend directly on this chemically known substance but on (III) (guinea-pig) derived therefrom *in vivo*. H. W.

Thiophenols. XIII. 3:3'-Dimethylthiolazobenzene and derivatives of 3-nitrophenyl methyl sulphide. K. BRAND and H. W. LEYERZAFF (Ber., 1937, 70, [B], 284–296).—Treatment of *m*-NO₂·C₆H₄·N₂Cl with CuCNS and KCNS at 0° gives a dark green cryst. compound of unascertained composition which readily evolves N₂ but gives 3-nitrothiocyanobenzene (I), m.p. 56°, in very small yield; better results are not obtained from *m*-NO₂·C₆H₄·N₂Cl, KCNS, and Cu powder. With *m*-NO₂·C₆H₄·N₂Cl and KCNS-CuCNS the yields are 30–53%. (I) is transformed by KOH-EtOH, by NH₃ followed by H₂S in EtOH, or by NH₃ in EtOH into 3:3'-dinitrodiphenyl disulphide (II), m.p. 84°, accompanied in the latter case by guanidine. Treatment of (II) with Na₂S and NaOH followed by Me₂SO₄ in EtOH leads to 3-nitrophenyl Me sulphide (III), m.p. 14.5°, converted by Me₂SO₄ into 3-nitrophenyldimethylsulphonium methosulphate, m.p. 140–141°, whence the corresponding

picrate, m.p. 163°, and iodide, m.p. 93°. 3-Nitrophenylthiolacetic acid, m.p. 136°, which is unchanged by short boiling with aq. NaOH, is obtained by the action of Na₂S and NaOH followed by CH₂Cl·CO₂H on (II). (III) is transformed by electrolytic reduction at a Ni gauze cathode or by NaOMe in MeOH into 3:3'-dimethylthiolazobenzene (IV), SMe·C₆H₄·NO·N·C₆H₄·SMe, m.p. 65–66°, transformed by Me₂SO₄ into the dimethylsulphonium methosulphate, whence the corresponding picrate, m.p. 175–176°, and iodide, SMe₂·I·C₆H₄·NO·N·C₆H₄·SMe₂·I, which regenerates (IV) when heated with MeOH. (IV) with Zn dust and CaCl₂ in boiling aq. EtOH affords 3:3'-dimethylthiolazobenzene (V), m.p. 103–104°, which in AcOH gives a yellow-orange solution transformed into brownish-violet by addition of fuming HCl, conc. H₂SO₄, or 70% HClO₄; it gives a complex salt with SnCl₄ but not with HgCl₂. (V) yields an unstable picrate and is converted into the dimethylsulphonium methosulphate, m.p. 163°, and the corresponding, unstable iodide which regenerates (V) when kept in a desiccator, boiled with EtOH, or heated. 3:3'-Dimethylthiolhydrazobenzene is transformed by HCl into 2:2'-dimethylthiolbenzidine, m.p. 207–208° (dihydrochloride, m.p. >270°; Ac₂, m.p. 235–236°, and Bz₂, m.p. 273–274°, derivatives). Gradual alternate addition of Fe powder and conc. HCl to (III) in EtOH containing CuCl₂ yields 3-aminophenyl Me sulphide, b.p. 163–165°/16 mm., converted by PhNO in EtOH-AcOH at 100° into 3-methylthiolazobenzene, m.p. 46°.

H. W.

Purification of diazoamino-compounds. F. P. DWYER (J.S.C.I., 1937, 56, 70–72r).—Pure cryst. diazoamino-compounds are obtained by treatment in hot aq. MeOH with Cd(OH)₂ which adsorbs the diazoaminoazo-compounds responsible for the red colour shown by the impure substances in alcoholic alkali. The colour of the ppt. is characteristic for Cd, which can be detected by *p*-nitrodiazoaminoazobenzene in presence of all common metals except Hg. The purification of diazoaminobenzene and its Me and Me₂ derivatives is described and a table showing the m.p. of 10 compounds is given. K. H. S.

Azo-group as a chelating group. II. Structure of diazoamino-compounds. L. HUNTER (J.C.S., 1937, 320–324).—By usual methods various compounds of the type NR:N·NHR' (I) and their N-substituted derivatives NR:N·NR'R' (II) are prepared, the following being new: *oo'*-dimethoxy-diazoaminobenzene, m.p. 97°; *γ*-phenyl-*α*-*m*-tolyl-*γ*-methyl-, m.p. 67°, *α*-*p*-bromophenyl-*γ*-dimethyl-, m.p. 62.5°, *γ*-phenyl-*γ*-methyl-, m.p. 82°, and *γ*-phenyl-*γ*-benzyl-, m.p. 111–112°, *α*-*o*-, m.p. 97–98°, and *α*-*p*-anisyl-*γ*-phenyl-*γ*-methyl-, m.p. 62°, -triazene. Cryoscopic determinations in C₆H₆ show that all compounds of type (I) have an association factor (α) > 1 which increases rapidly with increasing concn. (0–10% solution), but for those of type (II) α is slightly < 1 over an extended concn. range. Since only derivatives of type (I) exhibit that ambiguity of structure associated with tautomerism, dimeric resonance formulæ, both open-chain and cyclic, are suggested for (I), the most probable being that

involving the structures $N \begin{smallmatrix} \text{NR} \cdot \text{H} \cdot \text{NR}' \\ \text{NR}' \cdot \text{H} \cdot \text{NR} \end{smallmatrix} N$ and $N \begin{smallmatrix} \text{NR} \cdot \text{H} \cdot \text{NR}' \\ \text{NR}' \cdot \text{H} \cdot \text{NR} \end{smallmatrix} N$.

J. W. B.

Influence of solvent on the course of chemical reactions. XI. Allylation of sodium phenoxide in mixed solvents. K. LAUER and H. SHINGU (Ber., 1937, 70, [B], 326—333).—Measurements of the rate of reaction of NaOPh with allyl bromide in EtOH mixed with *n*-hexane, C₆H₆, PhMe, and tetrahydronaphthalene show the non-applicability of the Arrhenius equation, thus indicating two independent concurrent reactions. With diminishing dielectric capacity of the medium the rate of change declines owing to marked diminution of the action const. which exceeds the diminution of the energy of activation. With diminishing temp. the relative amount of *C*-allylation increases at the expense of *O*-allylation. The solubilities of many salts in abs. EtOH have been determined.

H. W.

Vlezenbeek's reaction on *p*-aminophenol derivatives. N. SCHOORL (Pharm. Weekblad, 1937, 74, 210—212).—The colour reactions obtained when *p*-NH₂·C₆H₄·OH derivatives are treated with *m*-C₆H₄(OH)₂ and H₂SO₄ are due to the formation of resorufin and resazurin.

S. C.

Identification and determination of thymol and carvacrol. Y. MAYOR (Parfum. Mod., 1937, 31, 5—11).—Identification, determination, and separation are described.

E. B. H.

Cumylphenol [4-hydroxy-ββ-diphenylprop-ane].—See B., 1937, 119.

Phenanthrene series. XIV. Preparation of 1- and 4-phenanthrol. E. MOSETTIG and H. M. DUVAL (J. Amer. Chem. Soc., 1937, 59, 367—369).—Dehydrogenation (Pd-black) of 1- and 4-keto-1:2:3:4-tetrahydrophenanthrene in C₁₀H₈ and xylene, respectively, gives 1- (68—86%) and 4-phenanthrol (56—63%), respectively. The use of other catalysts and solvents is investigated.

H. B.

Phenanthrene from 9-hydroxyphenanthrene. N. N. CHATTERJEE (J. Indian Chem. Soc., 1936, 13, 659).—This reaction is accomplished with Se at 300—330°.

R. S. C.

Synthesis in the phenanthrene series. V. 4-Methoxy-1-methylphenanthrene. A. HIGGINBOTTOM, P. HILL, and W. F. SHORT (J.C.S., 1937, 263—266).—By improved methods *p*-C₆H₄Me·NO₂ is converted successively into its 2-Br-derivative, 2-bromo-*p*-toluidine (Bz derivative, m.p. 132°), 2-bromo-*p*-cresol (benzoate, m.p. 74.5—75.5°), and 2-bromo-*p*-tolyl Me ether, the Mg compound (I) of which is converted by CO₂ into 4-methoxy-*o*-toluic acid, m.p. 142° (chloride, b.p. 125—126°/10 mm.), and by CH(OEt)₃ into 4-methoxy-*o*-tolualdehyde, b.p. 120°/11 mm. (semicarbazone, m.p. 212—213°), which could not be condensed with *o*-NO₂·C₆H₄·CH₂·CO₂Na. (I) with *p*-C₆H₄Me·SO₃·CH₂·CH₂Cl in C₆H₆ at 55° and subsequent hydrolysis gives β-(4-methoxy-*o*-tolyl)ethyl chloride, b.p. 132—133°/10 mm., the Grignard compound of which with cyclohexanone gives a mixture of αδ-di-(4-methoxy-*o*-tolyl)butane, b.p. 200—220°/5 mm.,

m.p. 105—106°, and 1-β-(4'-methoxy-*o*-tolyl)ethylcyclohexan-1-ol, b.p. 175—180°/4 mm., dehydrated by KHSO₄ at 160—170° to 1-β-(4'-methoxy-*o*-tolyl)ethyl-Δ¹-cyclohexene, b.p. 150—155°/4 mm. This with AlCl₃ in CS₂ at 0° gives a mixture, b.p. 130—162°/5 mm., dehydrogenated by S at 235° to a small yield of 4-methoxy-1-methylphenanthrene (II), m.p. 78.5—79° (picrate, m.p. 182—183°), converted by HI (*d* 1.7)—AcOH into 4-hydroxy-1-methylphenanthrene, m.p. 103—104° (Bz derivative, m.p. 121—122°). (I) and CH₂:CH·CH₂Br in Et₂O give 2-allyl-*p*-tolyl Me ether, b.p. 102—104°/10 mm., oxidised by KMnO₄-AcOH at 0° to 4-methoxy-*o*-tolylacetic acid, m.p. 103—104°, the K salt of which with *o*-NO₂·C₆H₄·CHO in Ac₂O at 100° gives 2-nitro-, m.p. 177—178°, reduced by FeSO₄-aq. NH₃ at 100° to 2-amino-α-(4'-methoxy-*o*-tolyl)cinnamic acid, m.p. 178—179°, converted by diazotisation into 4-methoxy-1-methylphenanthrene-10-carboxylic acid, m.p. 213.5—214°, decarboxylated to (II).

J. W. B.

Monoacetates of quinol and pyrocatechol. H. S. OLCOTT (J. Amer. Chem. Soc., 1937, 59, 392—393).—*O*-Carbobenzyloxy- (I), m.p. 120—120.5°, and *OO*-dicarbobenzyloxy- (II), m.p. 142—143°, -quinol are prepared from quinol (III) and ClCO₂CH₂Ph in aq. Na₂CO₃ and N₂. Acylation of (I) in C₅H₅N gives the Bz, m.p. 97—98°, and Ac, m.p. 75—76°, derivatives, which are cleaved by H₂ + Pt in EtOH to quinol monobenzoate and monoacetate (IV), m.p. 62—63°, respectively. (II) is similarly cleaved to (III). (IV) is more conveniently obtained [together with some *p*-C₆H₄(OAc)₂] from (III) and Ac₂O (1 equiv.) in aq. Na₂CO₃ (procedure: Chattaway, A., 1931, 1269); pyrocatechol monoacetate (V), b.p. 130—140°/0.1 mm., is similarly prepared. (V) is also obtained (as above) from the Ac derivative of *O*-carbobenzyloxy-pyrocatechol, m.p. 88.5—89°. All m.p. are corr. (V) is a more efficient antioxidant (towards lard) than (IV), but is much less active than either (III) or *o*-C₆H₄(OH)₂.

H. B.

Dissociable organic oxides. The photo-oxide C₁₆H₁₄O₄ of 9:10-dimethoxyanthracene. C. DUFRAISSE and R. PRIOU (Compt. rend., 1937, 204, 127—130).—On theoretical grounds, the photo-oxide C₁₆H₁₄O₄, m.p. 145° (decomp.), of 9:10-dimethoxyanthracene should dissociate more readily than the photo-oxide of 9:10-diphenylanthracene (cf. A., 1935, 1233), but, in fact, pyrolysis gives high yields of anthraquinone and no appreciable O₂.

J. D. R.

Mutual influence of radicals on their migration. II. Dehydration of phenyltert.-hexylcarbinol. A. E. FAVORSKI and P. A. TCHOMOLOV (Comp. rend. Acad. Sci. U.R.S.S., 1936, 4, 366—368; cf. A., 1936, 721).—Phenyltert.-hexylcarbinol, b.p. 130—130.5°/7 mm. [obtained by reduction (Na-EtOH) of the corresponding ketone], is converted by distillation from KHSO₄ into δ-phenyl-γ-methyl-Δ⁸-hexene, b.p. 91.75—92.5°/8 mm., which yields COMe·CHPhEt and MeCHO when ozonised. Comparison with the behaviour of phenyltert.-amylcarbinol (*loc. cit.*) suggests that group migration precedes dehydration.

F. N. W.

Benzoylmethylcarbinol and acetylphenylcarbinol. III. K. VON AUWERS (Biochem. Z., 1937,

289, 390—394; cf. A., 1928, 419).—The compound produced by interaction of PhCHO and MeCHO is CHPhAc·OH. Most of the supposed β -ketols are α -ketols. CHMeBz·OH gives CHPhAc·OH when distilled, boiled with H₂O and BaCO₃, or treated with alkali at room temp. and reacts slowly with NH₂·NH·CO·NH₂, giving the disemicarbazone of AcBz. Racemic CHPhAc·OH with NHPh·NH₂ gives the corresponding *phenylhydrazone*, m.p. 98—99°, or the phenylhydrazone of AcBz according to experimental conditions. W. McC.

Retention of asymmetry and inversion of configuration during anionotropic change. Conversion of (–) α -phenyl- γ -methylallyl alcohol into (+) γ -phenyl- α -methylallyl alcohol. J. KENYON, S. M. PARTRIDGE, and H. PHILLIPS (J.C.S., 1937, 207—218).—By fractional crystallisation of its quinaldine salt the *H* phthalate (I), m.p. 93—94°, of *dl*- α -phenyl- γ -methylallyl alcohol (II) (*p*-xenylurethane, m.p. 124°; *p*-nitrobenzoate, m.p. 99°; acetate, b.p. 135—136°/21.5 mm.) is resolved into the *H* phthalate (III), m.p. 81—82°, [α]₅₈₉₃ –17.1° in Et₂O [quinaldine salt, m.p. 146—147° (decomp.), [α]₅₈₉₃ +122.7° in CHCl₃], of (–) (IV), b.p. 126°/20 mm., α ₅₈₉₃ –34.17° (*l* 0.5) [*p*-xenylurethane, m.p. 120°, [α]₅₈₉₃ +20° in CHCl₃; acetate (V), b.p. 134—135°/20 mm.; *p*-nitrobenzoate (VI), [α]₅₇₉₀ –39.4° in CHCl₃], and the *H* phthalate, m.p. 80—81°, [α]₅₈₉₃ +15.5° in Et₂O [quinaldine salt, m.p. 133—134° (decomp.), [α]₅₈₉₃ +131.0° in CHCl₃], of (+)- α -phenyl- γ -methylallyl alcohol, b.p. 140°/20 mm., m.p. 33—34°, [α]₅₄₆₁ +2.2° in C₆H₅N. Although stable to alkalis (IV) is converted (*i*) with much racemisation in 0.5% aq. AcOH at room temp. into (+)CHPh·CH·CHMe·OH (VII) [*p*-xenylurethane obtained from (IV) with 87.7% retention of optical activity]. In agreement with Burton (A., 1928, 880) anionotropic interconversion occurs more readily with the esters of (IV) with retention of optical activity. Thus (V) in AcOH at room temp. and (VI) at 100° or in Ac₂O are converted, respectively, into (+) γ -phenyl- α -methylallyl acetate (*i*) and (–) γ -phenyl- α -methylallyl *p*-nitrobenzoate (*i*) [also from (VII) and NO₂·C₆H₄·COCl], but (VI) with AcOH gives (–) γ -phenyl- α -methylallyl acetate. Similarly (III) is converted (*i*) in presence or absence of solvents (unimol. *k* = 0.017 in CS₂; *E* in C₆H₆ = 28,800 g.-cal.) into (+) γ -phenyl- α -methylallyl *H* phthalate (VIII) with retention of >70% of the optical activity. Similar anionotropic conversions are effected with (I) and (II), and by conversion of (IV) into its derivatives. (III) is rapidly converted by EtOH or MeOH, respectively, into (–) γ -phenyl- α -methylallyl *Et*, b.p. 114°/11 mm., α ₅₈₉₃ –2.20° (*l*, 2), and *Me ether*, b.p. 124°/24 mm., α ₅₈₉₃ –0.34° (*l* 0.25), which is also obtained (*i*) by the slow action of MeOH on (VIII), or from MeOH and (VI), and differs from (+) γ -phenyl- α -methylallyl *Me ether*, b.p. 102—103°/10.5 mm., α ₅₈₉₃ +6.61° (*l* 0.25), obtained from the K derivative of (VII) and MeI. Reduction of (III) and (VII) gives, respectively, optically pure (+)OH·CHPhPr⁺ and (–)CH₂Ph·CH₂·CHMe·OH, whence the stereochemical relationships involved in these changes are deduced, those which involve inversion being denoted by (*i*). A mechanism involving the formation of a

cyclic configuration prior to anion migration is suggested. J. W. B.

Synthesis of drugs containing the phenanthrene nucleus. I. 2- and 3-Phenanthrylephe-drines. S. T. YANG and P. J. HSIEH (J. Chinese Chem. Soc., 1937, 5, 35—38).—With Br·AcOH 2-(*oxime*, m.p. 184—186°; semicarbazone, m.p. 201—202°) and 3-propionylphenanthrene (*oxime*, m.p. 119—120°; semicarbazone, m.p. 174—175°) yield the 2- and 3- α -Br-derivatives (cf. Bachmann *et al.*, A., 1936, 1380), which with NH₂Me give 2-, m.p. 240—241°, and 3- α -methylaminopropionylphenanthrene hydrochloride, m.p. 229—230°. Reduction of these in 95% EtOH with PtO₂–H₂/30—40 lb. per sq. in. gives, respectively, the hydrochloride, m.p. 241—243°, of 2-, m.p. 133—134°, and the hydrochloride, m.p. 182—183°, of 3-(β -methylamino- α -hydroxypropyl)phenanthrene, m.p. 103—104° (3-phenanthrylephe-drine). J. W. B.

Resolution of *trans*-cyclopentane-1:2-diol into its optically active components. B. HELFERICH and R. HILTMANN (Ber., 1937, 70, [B], 308—313).—An excess of *trans*-cyclopentane-1:2-diol, b.p. 99—101°/1.5 mm., m.p. 50—52°, is converted by aceto-bromoglucose (I) and dry Ag₂CO₃ into (? partly racemic) *trans*-cyclopentane-1:2-diol- β -D-monoglucoside tetra-acetate (II), m.p. 133.5—134.5° (corr.), [α]_D²⁰ –10.0° in CHCl₃, converted by further treatment with (I), Ag₂CO₃, and I in CHCl₃ free from EtOH into a product which when fractionally crystallised from MeOH yields d-*trans*-cyclopentane-1:2-diol- β -D-diglu-coside octa-acetate (III), m.p. 206.5—207.5° (corr.), [α]_D²⁰ –16.2° in CHCl₃, and l-*trans*-cyclopentane-1:2-diol- β -D-diglu-coside octa-acetate (IV), m.p. 189—190° (corr.) after softening at about 180°, [α]_D²⁰ –39° in CHCl₃. (II) is de-acetylated by NaOMe in MeOH to d-*trans*-cyclopentane-1:2-diol- β -D-glucoside (V), m.p. 102—104° (corr.; decomp.), [α]_D²⁰ –11.9° in H₂O. Similar treatment of (III) and (IV) leads to d- (VI), m.p. 200.5—201.5° (corr.), [α]_D²⁰ –29.8° in H₂O, and l- (VII), [α]_D²⁰ –56.3° in H₂O, -*trans*-cyclopentane-1:2-diol- β -D-diglu-coside. Fermentative fission of (V), (VI), and (VII) gives solutions of the corresponding diols for which [α]_D²⁰ +34.0° in H₂O and [α]_D²⁰ –33.8° in H₂O are thus calc. d-*trans*-cyclopentane-1:2-diol forms very hygroscopic crystals, m.p. 50—52°, [α]_D²⁰ +33.05° in H₂O. H. W.

Synthesis of methoxymethylbenzyl alcohols. R. QUELET and J. ALARD (Compt. rend., 1937, 204, 130—132).—*o*- and *m*-C₆H₄Me·OMe are converted by CH₂O and HCl gas into 4-methoxy-3- and -2-methylbenzyl chloride, respectively, converted by NaOAc and AcOH into the acetate and hydrolysed to 4-methoxy-3-methylbenzyl alcohol, b.p. 148—149°/18 mm. (*phenylurethane*, m.p. 90.5°), and 4-methoxy-2-methylbenzyl alcohol, b.p. 143—147°/18 mm. (*phenylurethane*, m.p. 71°). Similar treatment of thymol Me ether in presence of ZnCl₂ yields 4-methoxy-2-methyl-5-isopropylbenzyl alcohol, b.p. 165°/18 mm. (*phenylurethane*, m.p. 101°), and as a by product, 4:4'-dimethoxy-2:2'-dimethyl-5:5'-diisopropyldiphenylmethane, b.p. 230°/16 mm., m.p. 73°, oxidised by Na₂Cr₂O₇–AcOH to 4:4'-dimethoxy-2:2'-dimethyl-5:5'-diisopropylbenzo-phenone, m.p. 139°. J. D. R.

Thiophenols. XIV. Triphenylmethane series.
3-Methylthioltriphenylcarbinol. K. BRAND, W. GABEL, and E. ROSENKRANZ (Ber., 1937, 70, [B], 296—308).—The bathochromic action of SMe is closely similar to that of NMe₂ so that solutions of the salts of 4:4'-(SMe·C₆H₄)₂CPh·OH and 4:4':4''-(SMe·C₆H₄)₃C·OH have almost the same colour and the same absorption spectrum as malachite-green and crystal-violet. Since SMe is far less prone than NMe₂ to the formation of its "proper salts," compounds containing it are of particular importance for the constitution of the coloured salts of CAr₃·OH. Introduction of SMe at position 3 of CPh₃·OH diminishes the stability of the corresponding perchlorate towards hydrolysis whereas this property is enhanced when SMe is at 2 or 4. Introduction of SMe at 2 or 3 displaces the spectrum of CPh₃·OH, its perchlorate, and CHPh₃ towards longer λ . *m*-SMe·C₆H₄·NH₂, obtained from Na acetylmelanilate, is diazotised and treated with CuBr·KBr, thereby giving *m*-bromophenyl *Me* sulphide (I), b.p. 121°/14 mm., in moderate yield. *m*-CO₂H·C₆H₄·SO₂Cl in EtOH is reduced by Zn and HCl to 3:3'-dicarboxy-diphenyl disulphide, m.p. 246°, transformed by Na₂S and NaOH followed immediately by Me₂SO₄ into *m*-methylthiobenzoic acid, m.p. 126.5° [*Me* ester (II), b.p. 132°/4 mm.]. Treatment of (I) or of the corresponding iodide with activated Mg in Et₂O followed by C₆H₅Br or of (II) with MgPhBr in Et₂O yields non-cryst. *m*-methylthioltriphenylcarbinol (III), which yields a solid, additive compound with C₆H₆ but otherwise does not afford cryst. derivatives. Its solution in AcOH-H₂SO₄ or AcOH-HClO₄ exhibits a dull, yellowish-green halochromism indistinguishable by eye from that of *o*-SMe·C₆H₄·CPh₂·OH. (III) with Zn dust and Zn filings in boiling AcOH affords *m*-methylthioltriphenylmethane (IV), m.p. 49.5°, which gradually becomes greenish-yellow in AcOH-H₂SO₄ but is scarcely affected by conc. H₂SO₄. Optical data are given for (III), (IV), *m*-C₆H₄·Me·CPh₂·OH, and CHPh₂·C₆H₄·Me-*m*. H. W.

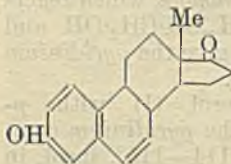
Acetylation decomposition of asarone- ψ -nitrosite. V. BRUCKNER and A. KRÁMLI (J. pr. Chem., 1937, [ii], 148, 5—12).—Asarone- ψ -nitrosite (A., 1933, 1289) with (a) Ac₂O-H₃PO₄ (*d* 1.75), or (b) Ac₂O-H₂SO₄, or (c) Ac₂O-H₂SO₄-H₃PO₄, gives a separable mixture of β -nitro- α -2:4:5-trimethoxyphenyl-*n*-propyl acetate (I), m.p. 102°, its stereoisomeride (II), m.p. 144°, and β -nitro- α -2:4:5-trimethoxyphenyl- Δ^2 -propene (III) (β -nitroasarone; *loc. cit.*). Methods (a) and (c) favour the formation of (II), whilst the proportion of (I) is increased in (b). (I), (II), or (IV) (below) when heated with EtOH-KOH and then acidified gives (III). When heated on a water-bath with COMe₂-10% H₂SO₄ (I) gives β -nitro- α -2:4:5-trimethoxyphenyl-*n*-propyl alcohol (IV), m.p. 91°. Electrolytic reduction at 40—50° of either (I) or (II) occurs with Ac migration to give β -acetamido- α -2:4:5-trimethoxyphenyl-*n*-propyl alcohol, +H₂O and anhyd., m.p. 163—164°. J. W. B.

Relations between optical rotatory power and constitution in the steroids. R. K. CALLOW and F. G. YOUNG (Proc. Roy. Soc., 1936, A, 157, 194—212).—Vals. (lit.) of $[\alpha]_D$ for various diastereoisomeric

pairs of sterols and related compounds are compared in order to see if regular changes in rotatory power are associated with inversion of 3-OH, 4-OH, 5-H, and 17-Ac. Similarly, various compounds containing 1:2-, 4:5-, 5:6-, 7:8-, 8:14-, 14:15-, or 22:23-double linkings are compared with those in which the corresponding linking is saturated. The following relationships appear to be established: (i) inversion of 3-OH from *cis* to *trans* (relative to 10-Me) is accompanied (in 15 out of 18 cases) by an increase in dextrorotatory power; (ii) increases in dextrorotation are caused by the 4:5- and 14:15- (less marked) double linkings; (iii) decreases in dextrorotation are associated with the 1:2-, 5:6-, and 22:23-double linkings. The conversion of 17-CO into CH·OH is accompanied by a decrease in dextrorotation. H. B.

Constitution of cholesterol. XIII. 13:18-Dimethyl-9:13-cyclopenteno-5:6-dehydrohydrophenanthr-3-ol from cholesterol. R. DE FAZI and F. PIRRONI (Atti R. Accad. Lincei, 1936, [vi], 23, 887—891).—The *sec.* alcohol, C₂₇H₄₆O, m.p. 202—203° (Ac derivative, m.p. 185—186°; Br₂-derivative, m.p. 164—165°), from cholesterol and CuCl (A., 1932, 510) probably has the above constitution. F. O. H.

Conversion of sterols into aromatic compounds. Conversion of cholesterol into isoequilin. H. H. INHOFFEN (Naturwiss., 1937, 25, 125—126).—Thermal decomp. of products obtained by fission of HBr from dibromoandrostanedione (from cholesterol) gives CH₄ and a phenol, C₁₅H₂₀O₂, m.p. 252° (decomp.), $[\alpha]_D^{25} +170^\circ$ in dioxan (absorption max. at 265, 275, and 334 m μ), which has weak physiological activity (Allen-Doisy) and is probably isoequilin, for which the annexed structure is suggested. J. W. B.



Constitution of lumisterol and of the product of the action of heat on vitamin-D₂ (calciferol). A. WINDAUS and K. DIMROTH (Ber., 1937, 70, [B], 376—379).—Ergosterol (I) is dehydrogenated by Hg(OAc)₂ to dehydroergosterol, which is also obtained from isopyrocalciferol (II) by treatment with cold Hg(OAc)₂ or BzO₂H. (I) and (II) differ therefore only by different steric arrangement at C₁₀. All other C atoms, particularly C₃ and C₁₀, have the same configuration and the double linkings are placed identically. Similarly, dehydrolumisterol, obtained from lumisterol (III), is also prepared from pyrocalciferol (IV). (III) and (IV) therefore differ only in the steric arrangement at C₁₀, the position of the double linkings and the configuration of all other C atoms being the same. (I) and (II) on the one hand and (III) and (IV) on the other hand differ in steric arrangement of Me at C₁₀. H. W.

Sterols. III. Toluenesulphonates of saturated sterols. IV. Sulphonic esters of unsaturated sterols. V. *allo*Cholesterol and its detection. VI. Isomerism of the two cholesteryl ethers. W. STOLL (Z. physiol. Chem., 1937, 246, 1—6, 6—10, 10—12, 13—14; cf. A., 1932, 737).—

III. Sulphonates of the non-precipitable saturated sterols are converted by boiling with MeOH during 2 hr. into unsaturated hydrocarbons and sulphonic acid (I) whereas esters of saturated sterols precipitable with digitonin give ethers and (I). The behaviour of the esters allows the parent sterol to be assigned to the cholestanol or epicholestanol series. The relative position of OH at C₍₃₎ and Me at C₍₁₀₎ appears to be the dominant factor whereas that of H at C₍₅₎ has little influence. The following *p*-toluenesulphonates are described: epicholestanyl, m.p. 124—125°, transformed by MeOH into $\Delta^{2:3}$ -cholestene, m.p. 69°, $[\alpha]_D^{20} + 64^\circ$ in CHCl₃; epiergostanyl, m.p. 140—142°, converted into a hydrocarbon, C₂₈H₄₈, m.p. 79—80°; epicoprosteryl, m.p. 116—118°. The rate of etherification of esters of precipitable sterols, measured by titration of the liberated acid, R·O·SO₂·C₆H₄Me + MeOH → ROme + C₆H₄Me·SO₃H, is > that of PhSO₃Me.

IV. The rates of reaction of cholesteryl, sitosteryl, and stigmasteryl *p*-toluenesulphonate with EtOH at 78° are high in comparison with those of the *p*-toluenesulphonates of 1 : 2 : 3 : 4-tetrahydro-2-naphthol, m.p. 85°, *cis-trans*-o-cyclohexenylcyclohexanol, m.p. 109—110°, and isopulegol, m.p. 95°, which vary so much among themselves that the assumption that cholesterol contains an $\alpha\beta$ -double linking is not justified, particularly since cholestanyl *p*-toluenesulphonate reacts readily. *p*-C₆H₄Me·SO₃Ag and CH₂:CH·CH₂Br yield non-cryst. allyl *p*-toluenesulphonate, which reacts rapidly with EtOH at 78°; CH₂:CH·CH₂OH and *p*-C₆H₄Me·SO₂Cl in C₅H₅N·CHCl₃ give the pyridinium compound, C₁₅H₁₇O₂NS, m.p. 97°.

V. Treatment of allocholesterol (I) with *p*-C₆H₄Me·SO₂Cl in C₅H₅N affords the pyridinium compound, C₃₀H₅₇O₃NS, m.p. about 114—115°, insol. in H₂O and Et₂O. By its means it is shown that the material known previously as (I) contains 50% of cholesterol (II) and is very probably a mol. compound of the true (I) and (II). The presence of (I) in bile, gall stones, liver, brain, or egg yolk could not be detected.

VI. Ozonisation of the normal cholesteryl Me ether (III) followed by distillation of the acidic products of the reaction gives the hydrocarbon, C₂₆H₄₂, m.p. 74—75°, $[\alpha]_D^{20} - 172^\circ$ in CHCl₃, of Windaus and Resau, showing that the double linking and OH are in the same position in (III) and in cholesterol. The isomeric, dextrorotatory cholesteryl Me ether (IV) is probably derived from allocholesterol. (IV) is hydrogenated to a new cholestyl Me ether (V) belonging to the cholestane series. Accordingly the two cholestyl Me ethers are either epimerides or OMe in (V) is not attached to C₍₃₎; this must then be true also for (IV).

H. W.

Marine products. IV. Sterols of the starfish. W. BERGMANN (J. Biol. Chem., 1937, 117, 777—781).—Asteriasterol isolated by Page (A., 1924, i, 120) from the starfish *Asterias forbesi* is a mixture of an alcohol closely resembling astrol and a less sol. sterol, m.p. 154—155°, $[\alpha]_D^{20} + 3.0^\circ$, resembling stellerol (I) but giving an acetate, m.p. 155—157°, $[\alpha]_D^{20} + 7.0^\circ$, a benzoate, m.p. 182°, and a 3 : 5-dinitrobenzoate, m.p. 194—195°, all melting very differently from the accepted vals. for (I) derivatives, together

with a more sol. sterol, m.p. 128—130°, $[\alpha]_D^{20} + 2.4^\circ$ (acetate, m.p. 128—130°; benzoate, m.p. 130—135°).

P. W. C.

Phytosterols. J. HADÁČEK and F. FINK (Časopis českoslov. Lék., 1935, 15, 206—212; Chem. Zentr., 1936, i, 2368).—A mono-unsaturated phytosterol, C₂₉H₅₀O, m.p. 134—135° (Ac compound, m.p. 120°, and its Br-derivative, m.p. 86°), is isolated from apricot oil.

H. N. R.

Activation of cholesterol and its derivatives.—See A., III, 156.

Photochemical transformation of ergosterol into vitamin-D.—See A., III, 155.

Sterols and carbohydrates in *Boletus edulis*.—See A., III, 161.

Normal long-chain acids terminating in cyclohexyl or cyclopentyl. I. cycloHexylvaleric acid and derivatives. M. KATZNELSON and B. BUBININ (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 405—408).—This acid (Tschischibabin, Chim. et Ind., 1932, 27, 563) gave a chloride, b.p. 139°/15 mm., amide, m.p. 122—123°, and Cd salt, solubility in H₂O 1.5%. The Et ester, b.p. 136—138°/12 mm., on reduction gave ϵ -cyclohexyl-n-amyl alcohol, b.p. 131—132°/11 mm. ϵ -cycloHexylamyl bromide, b.p. 124°/8.5 mm., on treatment of its Mg compound with furfuraldehyde, gave $\alpha\kappa$ -dicyclohexyldecane, m.p. 34°, and not the expected cyclohexylamylfurylcarbinol.

A. LI.

Anhydrides of naphthenic acids. M. P. GERTSCHUK and M. M. KATZNELSON (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 417—418).—cycloPentamethanecarboxylic anhydride, b.p. 157—158°/18 mm., and cyclohexanecarboxylic anhydride were prepared by treating the acid with (a) its acid chloride and C₅H₅N in the cold, or (b) Ac₂O at 140°; (a) gives better yields.

A. LI.

Preparation of *p*-bromobenzoic acid. M. C. CHIANG and C. L. TSENG (Sci. Rep. Nat. Univ. Peking, 1936, No. 4, 39—43).—An improved yield (83—88.9%) of *p*-C₆H₄Br·CO₂H is obtained by oxidation of *p*-C₆H₄MeBr with boiling aq. KMnO₄.

J. D. R.

Syntheses with iodo-silver nitrobenzoate complexes. R. JACQUEMAIN and A. MOSKOVITS (Compt. rend., 1937, 204, 134—136; cf. A., 1936, 843).—*o*-, *m*-, and *p*-NO₂·C₆H₄·CO₂Ag-I complexes convert C₂H₄ derivatives into the diesters of the corresponding glycols. From allyl *m*- and *p*-nitrobenzoate the following glycerol derivatives have been prepared by this method: α -*m*- β -*di*-*o*-, m.p. 133°, tri-*m*-, and α -*p*- β -*di*-*m*-, m.p. 157.5°, -nitrobenzoate. From CHPh:CH·CO₂Et, β -*di*-*o*-nitrobenzoate of Et β -phenylglycerate, m.p. 152°; from C₂H₄, glycol di-*o*-, m.p. 138°, di-*m*-, m.p. 130.5°, and di-*p*-, m.p. 145° -nitrobenzoate. The following are prepared by the Schotten-Baumann reaction: allyl *o*-, b.p. 167.5—169°, and *m*-, b.p. 169—170°, m.p. 20.5°, -nitrobenzoate; cinnamyl *o*-, m.p. 63°, *m*-, m.p. 59°, and *p*-, m.p. 75°, nitrobenzoate.

J. D. R.

Action of hydrogen cyanide on 4-methylcyclohexanone; preparation of the two stereoisomerides of 4-methylcyclohexanol-1-carboxylic acid.

M. GODCHOT and (MLE.) G. CAUQUIL (Compt. rend., 1937, 204, 77—79).—The NaHSO_3 compound of 4-methylcyclohexanone with KCN yields the cyanohydrin, hydrolysed by HCl to 4-methylcyclohexanol-1-carboxylic acid (I), m.p. 115° (*Me* ester, b.p. $107-108^\circ/14$ mm.; *amide*, m.p. $131-132^\circ$), and 4'-methyl- Δ^1 -cyclohexenyl 4-methylcyclohexanol-1-carboxylate, m.p. 119° , hydrolysed by KOH to 4-methylcyclohexanone and the stereoisomeride of (I), m.p. 82° (*amide*, m.p. 157° ; *Me* ester, b.p. $105^\circ/15$ mm.).

J. D. R.

6-Sulpho-*m*-cresotic acid and related compounds. A. N. MELDRUM and C. N. BAMJI (J. Indian Chem. Soc., 1936, 13, 641—644).—6-Sulpho-*m*-cresotic acid, $+4\text{H}_2\text{O}$, m.p. 93° [*K H*, $+3\text{H}_2\text{O}$, *Na H*, $+2\text{H}_2\text{O}$, *Ca H*, $+2.5\text{H}_2\text{O}$, and *Ba H*, $+2.5\text{H}_2\text{O}$, salts; *Me ether* (I), $+2\text{H}_2\text{O}$, m.p. 193° (decomp.)], obtained by Me_2SO_4 -NaOH or from *m*-cresotic acid *Me ether* and oleum at 60° , is obtained by sulphonation with 100% H_2SO_4 at room temp. Its constitution is proved by the following reactions. With fuming HNO_3 and oleum at room temp. it gives 2-nitro-, m.p. 85° (*Ba*, $+4\text{H}_2\text{O}$, and *Ca salt*, $+4\text{H}_2\text{O}$), and with Br in 45% HBr, best at 0° , gives 2-bromo-6-sulpho-*m*-cresotic acid (II), $+3\text{H}_2\text{O}$, m.p. 183° (*K H*, $+2\text{H}_2\text{O}$, and *Ca H salt*), but with fuming HNO_3 in conc. H_2SO_4 at $<0^\circ$ gives also some dinitro-*m*-cresotic acid, m.p. 185° , whereas at $>70^\circ$ (NO_2) $_3\text{C}_6\text{HMe}\cdot\text{OH}$, m.p. 105° , is formed; under other conditions (not detailed) it gives 6-nitro-*m*-cresotic acid by extrusion of the SO_3H . With steam in H_2SO_4 at 150° (II) gives 2-bromo-*m*-cresotic acid (III), m.p. 211° (*Na*, $+2\text{H}_2\text{O}$, and *K salt*), the *Me ether*, m.p. $137-138^\circ$ (*Ba salt*, $+2\text{H}_2\text{O}$), of which is obtained from (I) and Br in 40% HBr and which affords 2-bromo-6-nitro-*m*-cresotic acid by nitration (not detailed). Bromination of (II) in AcOH gives 2:6-dibromo-*m*-cresotic acid, but in dil. AcOH $\text{C}_6\text{HMeBr}_3\cdot\text{OH}$ is obtained. Gattermann's acid (A., 1893, i, 567) is (III).

R. S. C.

α -Hydroxyisobutyric acids. P. PREIFFER and A. DIEBOLD (J. pr. chem., 1937, [ii], 148, 24—34).— $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ (A., 1929, 822) when heated with aq. $\text{EtOH}\cdot(\text{NH}_4)_2\text{CO}_3$ -KCN and $\text{CO}_2/12$ atm. at 120° gives 5-benzyl-5-phenoxyethylhydantoin, m.p. 196° , hydrolysed by 25% KOH to α -amino-, m.p. $208-210^\circ$ (hydrochloride, m.p. $214-218^\circ$; *Bz* derivative, m.p. 163.5° ; *Cu salt*), converted by NaNO_2 -HCl into α -hydroxy- β -phenyl- α -phenoxyethylpropionic acid, m.p. $127-130^\circ$ (*Ac* derivative, m.p. 146° ; *Me* ester, m.p. $65-66^\circ$). The *Me* ester, b.p. $174^\circ/17$ mm., of *p*-anisiloxycetic acid (Kollsch, A., 1931, 345) and $\text{CH}_2\text{Ph}\cdot\text{CN}\cdot\text{NaOEt}\cdot\text{EtOH}$ afford α -(*p*-anisiloxycetyl)phenylacetone, m.p. $106-107^\circ$, hydrolysed by AcOH-HCl at room temp. to the *amide*, m.p. 158° , hydrolysed by boiling 8% HCl to benzyl *p*-anisiloxymethyl ketone, b.p. $210-216^\circ/12$ mm., m.p. $48.5-49.0^\circ$ [oxime, m.p. $69-70^\circ$; semicarbazone, m.p. 143° ; oximino-derivative, m.p. 189° (decomp.)]. This is converted (as above) into 5-benzyl-5-*p*-anisiloxymethylhydantoin, m.p. 189.5° , hydrolysed by boiling 40% KOH to α -amino-, m.p. 218° (decomp.) (*Ac* derivative, m.p. 198.5° ; *Cu salt*), converted by HNO_2 into α -hydroxy- β -phenyl- α -*p*-anisiloxymethylpropionic acid, m.p. 135.5° . J. W. B.

Derivatives of 1-hydroxy-2-naphthoic acid. I. 4-Halogeno-1-hydroxy-2-naphthoic acids and their derivatives. G. V. JADHAV, S. N. RAO, and N. W. HIRWE. II. 4-Halogeno-1-methoxy-2-naphthoic acids and their derivatives. G. V. JADHAV and S. N. RAO (J. Indian Chem. Soc., 1936, 13, 609—612, 645—648).—I. 1:2- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ resembles $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ in that its 4-halogeno-derivatives (prep. from the 4- SO_3H -compound) readily give the acid chloride with PCl_5 , the aryl esters from the acid, phenol, and POCl_3 at $140-150^\circ$, the alkyl esters from the Ag salt and alkyl iodide or the chloride and alcohol, and the arylamide from the chloride and base. Thus are obtained 4-bromo-, m.p. $240-241^\circ$ (chloride, m.p. $118-119^\circ$; *Na*, $+2.5\text{H}_2\text{O}$, and *K salt*; *Ph*, m.p. $104-105^\circ$, $\beta\text{-C}_{10}\text{H}_7$, m.p. $183-184^\circ$, *Me*, m.p. $121-122^\circ$, and *Et* ester, m.p. $86-87^\circ$; *anilide*, m.p. $164-165^\circ$; *o*-, m.p. $164-165^\circ$, *m*-, m.p. $202-203^\circ$, and *p*-toluidide, m.p. $150-151^\circ$), and 4-chloro-1-hydroxy-2-naphthoic acid, m.p. $232-233^\circ$ (chloride, m.p. $121-122^\circ$; *K salt*; *Ph*, m.p. $103-104^\circ$, $\beta\text{-C}_{10}\text{H}_7$, m.p. $186-187^\circ$, *Me*, m.p. $120-121^\circ$, and *Et* ester, m.p. $92-93^\circ$; *anilide*, m.p. $180-181^\circ$; *o*-, m.p. $148-149^\circ$, *m*-, m.p. $188-189^\circ$, and *p*-toluidide, m.p. $143-144^\circ$), both giving $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ with HNO_3 (*d* 1.16).

II. 4-Halogeno-1-hydroxy-2-naphthoic acids cannot be methylated by Me_2SO_4 -NaOH. Halogenation of 1:2- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{Me}$ (modified prep.) gives 4-bromo-, m.p. $196-197^\circ$ (chloride, m.p. $114-115^\circ$; *Ph*, m.p. $88-89^\circ$, $\beta\text{-C}_{10}\text{H}_7$, m.p. $114-115^\circ$, *Et*, m.p. $78-79^\circ$, and *Me* ester, m.p. $96-97^\circ$; *anilide*, m.p. $123-124^\circ$; *o*-, m.p. $142-143^\circ$, *m*-, m.p. $122-123^\circ$, and *p*-toluidide, m.p. $143-144^\circ$), and 4-chloro-1-methoxy-2-naphthoic acid, m.p. $182-183^\circ$ (chloride, m.p. $106-107^\circ$; *Ph*, m.p. $74-75^\circ$; $\beta\text{-C}_{10}\text{H}_7$, m.p. $112-113^\circ$, *Et*, m.p. $77-78^\circ$, and *Me* ester, m.p. $83-84^\circ$; *anilide*, m.p. $105-106^\circ$; *o*-, m.p. $134-135^\circ$, *m*-, $116-117^\circ$, and *p*-toluidide, m.p. $113-114^\circ$), the structure of which is proved by demethylation.

R. S. C.

Preparation of hexahydroterephthalic acid. G. KOMPPA and W. ROHRMANN (Ann. Acad. Sci. fenn., 1935, 41, No. 8, 5 pp.; Chem. Zentr., 1936, i, 2339—2340).— $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ is only incompletely hydrogenated with Skita's Pt at $50-60^\circ/3$ atm. Similarly $p\text{-C}_6\text{H}_4(\text{CO}_2\text{Me})_2$ takes up only $\frac{2}{3}$ of the theoretical amount of H_2 at $50-60^\circ/3$ atm. in MeOH. A procedure for removing unhydrogenated material is described.

H. N. R.

Syntheses from ethanolamine. IV. Synthesis of *N*- β -chloroethylphthalimide. H. WENKER (J. Amer. Chem. Soc., 1937, 59, 422).— $o\text{-C}_6\text{H}_4(\text{CO}_2)_2\text{O}$ and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ at 210° give a quant. yield of *N*- β -hydroxyethylphthalimide, m.p. $127-128^\circ$, converted by PCl_5 into *N*- β -chloroethylphthalimide, m.p. 81° .

H. B.

Permonophthalic acid and its application in place of perbenzoic acid as an oxidising agent. H. BÖHME (Ber., 1937, 70, [B], 379—383).—Finely divided $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ is added to 15% NaOH and 30% H_2O_2 which have been cooled in ice and salt and then mixed. After nearly complete dissolution the mixture is poured into 20% H_2SO_4 at -10° and

immediately filtered through glass wool. The filtrate is extracted with Et_2O and the extract is washed with 40% $(\text{NH}_4)_2\text{SO}_4$ and dried over Na_2SO_4 . The solutions are generally more stable than those of BzO_2H . At 0° , the titre declines somewhat markedly during the first few days and subsequently by about 0.2% per day. They are well adapted to the determination of the ethylenic linking, of sulphides, and of sulphoxides at 10 – 15° particularly when the reagent is used in relatively large excess. Preparatively permonophthalic acid has the advantage over BzO_2H that the o - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ formed is very sparingly sol. in CHCl_3 . As examples, $\text{CH}_2\text{Cl}\cdot\text{SEt}$ is oxidised to the sulphone and $(\text{CH}_2\text{Ph})_2\text{S}$ to the sulphoxide.

H. W.

Pechmann dyes. Synthesis which introduces dissimilar substituents. P. CHOVIN (Compt. rend., 1937, 204, 360–363).— $\text{CH}_2\text{Bz}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ with β -*p*-toluoylpropionic acid under von Pechmann's conditions (1882) affords a dye, m.p. 307° , also obtained from *p*-toluoylpyruvic acid and $\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which indicates that the structure of the chromophore group is symmetrical.

J. L. D.

"Di(phenylpyruvic acid)"; preparation of phenylbenzylsuccinic acids. J. JARROUSSE (Compt. rend., 1937, 204, 132–134).— $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{Me}$ with K_2CO_3 yields the lactone of γ -hydroxy- α -keto- γ -carbomethoxy- $\beta\delta$ -diphenylbutyric acid (I), saponified by NaOH to so-called di(phenylpyruvic acid), i.e., α -hydroxy- α' -keto- β -phenyl- α -benzylglutaric acid. Saponification of (I) in neutral solution yields a mixture of distereoisomerides of phenylbenzylsuccinic acid, separated by their Ca salts, m.p. 183° [anhydride, m.p. 73° (II); Me_2 ester, m.p. 85°] and m.p. 215° [anhydride, m.p. 92° , converted at 100° into (II); Me_2 ester, m.p. 124°].

J. D. R.

Sterol group. XXVIII. Application of Reformatsky reaction to 7-ketocholesteryl acetate: Δ^5 -cholestene-3:7-diol-7-acetic acid. E. R. H. JONES and F. S. SPRING (J.C.S., 1937, 302–304).—7-Ketocholesteryl acetate with $\text{Zn}\cdot\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 gives a mixture from which is isolated 3:7-dihydroxy- Δ^5 -cholestene-7-acetic acid, m.p. 161° (decomp.) [Me ester, m.p. 161 – 161.5° , $[\alpha]_D^{20}$ -49.1° in CHCl_3 (3-Ac, m.p. 136° , $[\alpha]_D^{20}$ -62.3° in CHCl_3 , and 3-Bz, m.p. 158° , $[\alpha]_D^{20}$ -14° in CHCl_3 , derivatives)], converted by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ at 100° into 3-acetoxy- Δ^5 -cholesterylidene-7-acetic acid, m.p. 216 – 217° (decomp.), $[\alpha]_D^{20}$ -334.6° in CHCl_3 (absorption max. 2680 Å ; $\log \epsilon = 4.16$), whereas boiling Ac_2O affords 7-methylencholesterol.

J. W. B.

Transformation of dehydrodeoxycholic acid into α - and β -3-hydroxy-12-ketocholanic acid in the organism of the toad. K. KYOCOKU (Z. physiol. Chem., 1937, 246, 99–105).—Dehydrodeoxycholic acid (I) is hydrogenated (PtO_2) in neutral or alkaline solution mainly to α -3-hydroxy-12-ketocholanic acid (II), m.p. 165° (*Et* ester, m.p. 138°). In acid medium (I) yields predominately β -3-hydroxy-12-ketocholanic acid (III), m.p. 220° , identical with the product isolated from the urine of toads (A., 1935, 749, 1237). The acid, m.p. 125° , obtained from the same source is a difficultly separable mixture

of (II) and (III) as shown by its production by catalytic reduction of (I) in AcOH and by the admixture of (II) and (III) in suitable proportion. The possibility of epimerisation of OH at C_{13} in the animal organism is thus established and reasons are advanced for considering that it occurs by oxidation to CO followed by reduction.

H. W.

Manufacture of diamides and imides of aromatic dicarboxylic acids.—See B., 1937, 120.

Syntheses in the phenanthrene series. IV. 1-Methoxy-2-methylphenanthrene and the preparation of substituted phenylacetic acids. P. HILL and W. F. SHORT (J.C.S., 1937, 260–263).—The anilide, b.p. about $210^\circ/8\text{ mm.}$, m.p. 82.5 – 83° , of 2-methoxy-*m*-toluic acid (by methylation of 2:1:3-OH- $\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$) is converted through the iminochloride, and the hydrazide, m.p. 79.5 – 80.5° , through the benzenesulphonhydrazide, m.p. 149 – 150° , by the method of McFayden *et al.* (A., 1936, 850), into 2-methoxy-*m*-tolualdehyde. This with $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}\cdot\text{Ac}_2\text{O}\cdot\text{NaOH}$ affords 2-phenyl-4-(2'-methoxy-*m*-tolylidene)oxazolone, m.p. 160 – 161° , hydrolysed by boiling 10% NaOH to 2-methoxy-*m*-tolyl-pyruvic acid, m.p. 131 – 132° , oxidised by 6% H_2O_2 –10% aq. NaOH at 0° to the acetic acid (I), m.p. 98.6 – 99.6° . The K salt of this with o - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in Ac_2O at 100° gives 2-nitro- α -(2'-methoxy-*m*-tolyl)cinnamic acid, dimorphous, m.p. 180 – 181° , and m.p. 198 – 199° , reduced by FeSO_4 –aq. NH_3 to the 2- NH_2 -acid, m.p. 188 – 188.5° , cyclised by diazotisation and heating with Na_2CO_3 to 1-methoxy-2-methylphenanthrene-10-carboxylic acid, m.p. 186.3 – 187.3° , decarboxylated by Cu powder in quinoline at 230° to 1-methoxy-2-methylphenanthrene (II), m.p. 82.5 – 83° (picrate, m.p. 127.5 – 128°). (II) with $\text{CrO}_3\cdot\text{AcOH}$ at $<70^\circ$ gives 2-methylphenanthrene-1:4-quinone, m.p. 153 – 154° , converted by $\text{Zn}\cdot\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ into 1:4-diacetoxy-2-methylphenanthrene, m.p. 165 – 165.5° . Rearrangement of *o*-tolyl allyl ether and methylation gives 3-allyl-*o*-tolyl Me ether, b.p. 94 – $96^\circ/10\text{ mm.}$, oxidised by 5% KMnO_4 at $<1^\circ$ to (I). Similar oxidation of 3-allyl-*p*-tolyl Me ether (from the 3-MgBr compound and $\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\text{Br}$) gives 4-methoxy-*m*-tolylacetic acid, m.p. 131 – 132° .

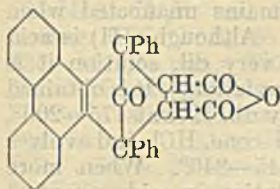
J. W. B.

Condensation of ethyl ethylideneacetoacetate in presence of sulphuric acid. B. CIOCCA and (SIGNA.) M. SCATTOLA (Gazzetta, 1936, 66, 776–779).— $\text{CHMe}\cdot\text{CAc}\cdot\text{CO}_2\text{Et}$ and H_2SO_4 react violently to form the Et ester (cf. A., 1936, 1249) of 2:6-dimethyl- Δ^2 -cyclohexen-4-one-1-carboxylic acid, m.p. ($+0.5\text{ H}_2\text{O}$) 60° , (anhyd.) 75 – 76° (decomp. to the ketone) (*Ba* salt) and Et, 2:4-dimethyl- Δ^4 -cyclohexen-6-one-1:3-dicarboxylate (*loc. cit.*), with resins.

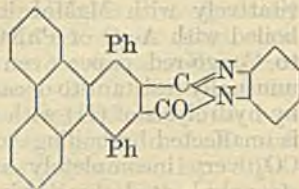
E. W. W.

Heteropolarity. XXVIII. Maleic acid adducts to phencyclone. W. DILTHEY, I. TER HORST, and A. SCHAEFER (J. pr. Chem., 1937, [ii], 148, 53–71).—2:5-Diphenyl-3:4-(2:2'-diphenylene)- Δ^2 :4-cyclopentadienone (I) (A., 1935, 1241) and maleic anhydride in boiling PhCl give 3:6-endocarbonyl-3:6-diphenyl-4:5-(2:2'-diphenylene)-1:2-dihydrophthalic anhydride (II), m.p. 286 – 287° (decomp.), hydrolysed by 50% $\text{KOH}\cdot\text{EtOH}$ to the free cis-acid,

m.p. 277—278° [also from (I) and maleic acid], and an acid, $C_{33}H_{24}O_6$, m.p. 215°, and converted by



(II.)



(IV.)

heating with the appropriate amine into the *anil*, m.p. 293—294°, *p*-tolyl-, m.p. 270—271° (decomp.), *p*-dimethylaminophenyl-, m.p. 296—298°, and *p*-diphenyl-, m.p. 273° (decomp.), *-imide*. When heated in $C_{10}H_8$ (II) gives a small yield of 3:6-diphenyl-4:5-(2:2'-diphenylene)-1:2-dihydrophthalic anhydride, m.p. 298—300°, but simple fusion or heating in S or $PhNO_2$ causes complete dehydrogenation to 3:6-diphenyl-4:5-(2:2'-diphenylene)phthalic anhydride (III), m.p. 348—350° [corresponding acid, m.p. 330—335° with conversion into (III)]. From (III) and the appropriate amine are obtained the *anil*, m.p. 358°, *p*-tolyl-, m.p. 341°, *p*-dimethylaminophenyl-, m.p. 338°, and *p*-aminodiphenyl-, m.p. 361°, *-imide*. (III) gives a condensation product (IV), m.p. 312°, with o - $C_6H_4(NH_2)_2$, and 3:6-diphenyl-4:5-(2:2'-diphenylene)phthaloperinone [as (IV)], m.p. 319°, with 1:8- $C_{10}H_6(NH_2)_2$. The colour reactions of these derivatives are tabulated. When heated with $AlCl_3$ in C_6H_6 (III) gives 2-phenyl-3:4-(2:2'-diphenylene)fluorenone-1-carboxylic acid, m.p. 312°, converted by a large excess of $AlCl_3$ in very small yield into the difluorenone (V), m.p. 321°.



(V.)

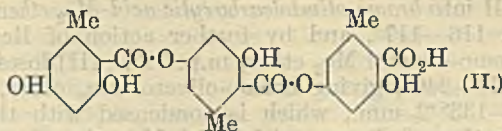
J. W. B.

Phthalide formation. P. K. PAUL (J. Indian Chem. Soc., 1936, 13, 599—601).—Gallic acid Me_3 ether, 40% CH_2O , and fuming HCl in $AcOH$ at 100° give 3:4:5-trimethoxy-2-chloromethylphthalide, m.p. 86°, converted by KCN in hot $EtOH$ into the cyanomethyl derivative, m.p. 103°, and thence into 3:4:5-trimethoxyphthalide-2-acetic acid, m.p. 126°. Myristic acid gives similarly the chloro-, m.p. 133—134°, and cyano-methylphthalide, m.p. 146—147°, and phthalideacetic acid, m.p. 211—212°, but in H_2O affords a methoxymethylenedioxyphthalide, m.p. 181°; the orientation in this series is uncertain.

R. S. C.

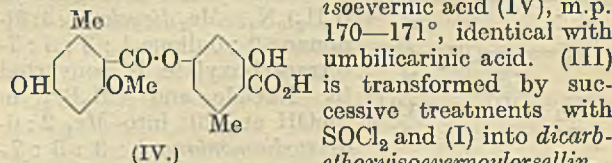
Lichen substances. LXXV. Syntheses of gyrophoric acid. II. Umbilicaric and umbilicaric acid. Y. ASAHINA and I. YOSIOKA (Ber., 1937, 70, [B], 200—206).—Lecanoric acid is converted by $ClCO_2Et$ in C_6H_5N at -15° into tri-carbethoxylecanoric acid, m.p. 137—138° (decomp.), the chloride of which is transformed by orsellinaldehyde (I) in $Et_2O-C_5H_5N$ into tricarbethoxylecanoroyl-orsellinaldehyde, m.p. 146° after softening at 140°, which with $ClCO_2Et$ affords tetracarbethoxylecanoroyl-orsellinaldehyde, m.p. 101°, oxidised by $KMnO_4$ in $COMe_2$ at 45° to tetracarbethoxylecanoroyl-orsellinic acid, m.p. 146° (decomp.), identical with tetracarbethoxygyrophoric acid and hydrolysed to gyro-

phoric acid, m.p. 220° (decomp.), which is therefore (II). Triacetyl-lecanoric acid, m.p. 195° (*Me* ester,



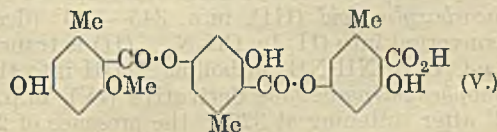
(II.)

m.p. 159.5°), similarly affords triacetyl-lecanoroyl-orsellinaldehyde, m.p. 159—161°, whence (by Ac_2O in Et_2O containing anhyd. K_2CO_3) tetra-acetyl-lecanoroyl-orsellinaldehyde, m.p. 190° after softening at about 187°, oxidised to tetra-acetylgyrophoric acid, m.p. 226°, which is de-acetylated with difficulty. isoeverninaldehyde is converted into carbethoxyisoeverninaldehyde, m.p. 63—64°, which is oxidised to carbethoxyisoeverninic acid, m.p. 111—111.5°, more conveniently obtained from carbethoxyorsellinic acid by treatment with Ag_2O and MeI and subsequently with conc. H_2SO_4 . The corresponding chloride is condensed with (I) to carbethoxyisoevernoyl-orsellinaldehyde, m.p. 131°, transformed by successive carbethoxylation and oxidation into dicarbethoxyisoeverninic acid (III), m.p. 101°, which is hydrolysed to isoeverninic acid (IV), m.p. 170—171°, identical with umbilicaric acid. (III) is transformed by successive treatments with $SOCl_2$ and (I) into dicarbethoxyisoevernoyl-orsellinaldehyde (corresponding *p*-nitrophenylhydrazone softens at 140°), converted into tricarbethoxyisoevernoyl-orsellinaldehyde, softens at 120°, whence tricarbethoxy-



(IV.)

isoevernoyl-orsellinic acid, m.p. 138—139° (decomp.), hydrolysed to isoevernoyl-orsellinic acid (V), m.p. 189° (Ac_3 derivative, m.p. 193—194°, and its *Me* ester, m.p. 206°), identical with umbilicaric acid.



(V.)

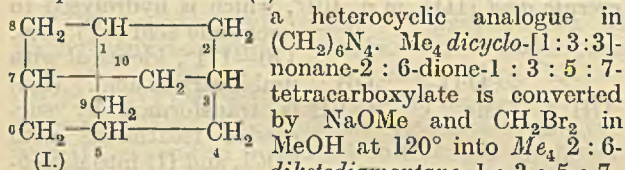
H. W.

Lichen substances. LXXVI. Constitution of lobaric acid. III. Y. ASAHINA and M. YASUE (Ber., 1937, 70, [B], 206—209).—The presence of the Ph_2O skeleton in lobaric acid is established. Lobaric acid Me_2 ether is decarboxylated by Cu chromite in quinoline at 190° to decarboxylobaric acid Me_2 ether [2:4:3'-trimethoxy-5'-valeryl-6-n-amyldiphenyl ether], b.p. 205—210°/0.01 mm., converted by the successive action of $N_2H_4 \cdot H_2O$ and KOH at 140° into protolobaric acid Me_2 ether [2:4:3'-trimethoxy-6:5'-di-n-amyldiphenyl ether], b.p. 190—195°/0.01 mm. (tribromide, m.p. 97—98°). Olivetol is transformed by HCN and HCl in Et_2O into the corresponding aldehyde, m.p. 66—67°, which is carbethoxylated, oxidised, and then decarbethoxylated to olivetolcarboxylic acid, m.p. 142°. This is treated successively with CH_2N_2 and Ag_2O-MeI and then decarboxylated to olivetol Me ether (I), b.p. 130°/2 mm. Olivetol Me_2 ether is transformed by $HCN-AlCl_3-HCl$ into the corresponding aldehyde, b.p. 143—146°/2 mm. (semicarbazone,

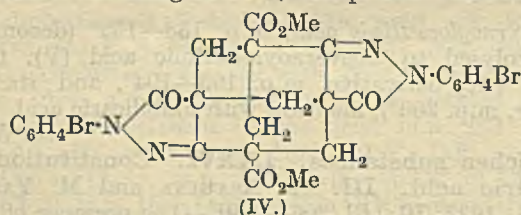
m.p. 149–150°), which is oxidised to *olivetolcarboxylic acid* Me_2 ether, m.p. 52–53°, transformed by Br into AcOH into *bromo-olivetolcarboxylic acid* Me_2 ether (II), m.p. 116–117°, and by further action of Br into dibromo-olivetol Me_2 ether, m.p. 72°. (II) loses CO_2 at 220–240°, giving bromo-olivetol Me_2 ether, b.p. 129–133°/2 mm., which is condensed with the K derivative of (I) to *protolobarol* Me_3 ether [2:4:3'-trimethoxy-5':6-di-n-amyldiphenyl ether], b.p. 180–190°/0.01 mm.; this gives a Br_3 -derivative, m.p. 97–98°, identical with tribromoprotolobarol Me_3 ether.

H. W.

Organic compounds of "diamondoid" structure. O. BÖTTGER (Ber., 1937, 70, [B], 314–325).—"Diamondoid" substances are those containing the C atoms in the mol. corresponding with the C-atom lattice of diamond. The description is limited to compounds which according to the tetrahedral theory are completely free from strain and belong to the hydroaromatic series and excludes compounds in which, as in *cyclohexane*, there is a possibility of transition between different strain-free, steric forms. The parent substance (I) is termed *diamontane* and finds



tetracarboxylate (II), m.p. 283.5–284.5°. This is stable towards Br, insol. in cold alkali, does not give a colour with FeCl_3 , contains 4 OMe (Zeisel), and is hydrolysed by acids to 2:6-diketodiamontane-1:3:5:7-tetracarboxylic acid (III), m.p. 345–346° (decomp.), re-converted into (II) by CH_3N_2 . (II) is transformed by $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$ in boiling AcOH into the *di-p-bromophenyldipyrazolone* derivative (IV), m.p. 331–332° after softening at 329°; the presence of 2 CO in



β -position to CO_2Me is confirmed by the hydrogenation (Pt on SiO_2) of (III) to 2:6-dihydroxydiamontane-1:3:5:7-tetracarboxylic acid (V), decomp. about 310° when rapidly heated, but converted into a mass, m.p. >375°, when heated slowly, the Me_4 ester (VI), m.p. 237.5–239°, of which contains 2 OH (Zerevitinov). The action of alkali on (II) proceeds somewhat indefinitely and under apparently identical conditions gives different products; under defined conditions (II) is hydrolysed and then converted by CH_3N_2 into Me_5 dicyclo-[1:3:3]-nonan-9-one-1:3:3:5:7-pentacarboxylate, m.p. 143–143.5°, re-transformed into (II) and MeOH when heated. Prolonged treatment of (III) with Zn-Hg and boiling HCl proceeds only to 2-hydroxydiamontan-6-one-1:3:5:7-tetracarboxylic acid (Me_4 ester, m.p. 177.5–178.5°). Attempted reduction of (V) by P

and HI at 180° gives unchanged material and unrecognisable products. Although (VI) reacts quantitatively with MgMeI it remains unaffected when boiled with Ac_2O or PhNCO . Although (III) is acid to Congo-red paper even in very dil. solution it is unusually resistant to decarboxylation. It is obtained by hydrolysis of (II) with very dil. HCl at 175–200°, is unaffected by boiling AcOH-conc. HCl, and evolves CO_2 very incompletely at 345–346°. When more strongly heated alone or in solution, in acid or neutral medium it becomes carbonised and dry distillation with $\text{Ba}(\text{OH})_2$ or ignition of the Ag_4 salt gives ill-defined products. The possible existence of optical isomerides in the *diamontane* series is discussed.

H. W.

Action of Raney's nickel on some aldoximes. R. PAUL (Compt. rend., 1937, 204, 363–365).—The oximes of MeCHO , PhCHO , furfuraldehyde, and cinnamaldehyde with Raney's Ni in boiling Et_2O , or at 100°, afford the corresponding amides (cf. A., 1927, 648; 1933, 700) and a little of the original aldehydes.

J. L. D.

Manufacture of nitrogenous aromatic aldehydes.—See B., 1937, 120.

Reactions catalysed by aluminium chloride.

XVI. Structure of the ketone obtained from methylcyclohexane and acetyl chloride. C. D. NENITZESCU, E. CIORANESCU, and I. P. CANTUNIARI (Ber., 1937, 70, [B], 277–283).—Condensation of methylcyclohexane (I) with AlCl_3 and AcCl occurs in the same manner as with *cyclohexane*, an equilibrium between (I) and the corresponding cyclopentane derivative (II) being established which is greatly in favour of (I). Further action takes place exclusively with (II) so that no 6-ring ketone is produced. (I), AcCl , and AlCl_3 at room temp. give unchanged material, the hydrocarbon $\text{C}_{14}\text{H}_{26}$, and 1-acetyl-2:3-dimethylcyclopentane (III), b.p. 182–184°/754 mm. (semicarbazone, m.p. 152°), with small amounts of 2-acetyl-1-methylcyclopentane (semicarbazone, m.p. 165°). (III) is reduced (Clemmensen) to 2:3-dimethyl-1-ethylcyclopentane, b.p. 141–143°, which is not dehydrogenated by Pt-C at 310°, thus establishing the absence of a 6-membered ring, whereas it is converted by Na in $\text{MeOH}\cdot\text{H}_2\text{O}\cdot\text{Et}_2\text{O}$ into 2:3-dimethyl-1- α -hydroxyethylcyclopentane, b.p. 79–81°/13 mm., 186–188°/760 mm. Oxidation of (III) by NaOBr gives 2:3-dimethylcyclopentane-1-carboxylic acid (II), b.p. 131°/18 mm. [corresponding chloride (V), b.p. 78–80°/18 mm., 183–185°/760 mm., and amide, m.p. 170°], which when treated successively with HN_3 in C_6H_6 and $\text{NaOH}\cdot\text{BzCl}$ gives 1-benzamido-2:3-dimethylcyclopentane, m.p. 113°. (V) is transformed by NH_2Me in $\text{C}_6\text{H}_5\text{N}\cdot\text{Et}_2\text{O}$ into 2:3-dimethylcyclopentane-1-carboxymethylamide, b.p. 149–152°/18 mm., m.p. 82°, converted by the successive action of PCl_5 in C_6H_6 and H_2O into 1-chloro-2:3-dimethylcyclopentane-1-carboxymethylamide, b.p. 128–134°/15 mm., showing that CO_2H of (IV) is not attached to a quaternary C (the validity of the method in the cyclopentane series is established by the conversion of 2-methylcyclopentane-1-carboxymethylamide, b.p. 145–147°/15 mm., m.p. 78°, into 1-chloro-2-methylcyclopentane-1-carboxymethylamide, b.p. 120–

122°/15 mm.). (IV) is obtained synthetically as follows. $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ is condensed with $\text{CNaMeAc}\cdot\text{CO}_2\text{Et}$ and the product is hydrolysed by boiling HCl (1:2) to β -methyl-lævulic acid, b.p. 137—145°/15 mm. This with Na-Hg and H_2O gives β -methyl- γ -valerolactone, b.p. 210°, converted by Na in abs. EtOH into γ -methylpentane- β -diol, b.p. 134°/20 mm. Saturation of the glycol in Ac_2O with HBr affords β -dibromo- γ -methylpentane, b.p. 105—107°/20 mm., which with $\text{CHNa}(\text{CO}_2\text{Et})_2$ gives *Et*₂ 2:3-dimethyleyclopentane-1:1-dicarboxylate, b.p. 147—149°/20 mm. (I) is much less stable than its lower homologue towards AlCl_3 , which is more active when somewhat moist than when completely dry. At its b.p. it gives gaseous hydrocarbons, mainly isobutane, in considerable amount; the olefines produced simultaneously become polymerised and deposited on the AlCl_3 . The residual, saturated equilibrium mixture contains about 99% of (I). At 130° the equilibrium mixture has the same composition but decomp. into gaseous hydrocarbons is much more extensive. H. W.

Synthesis of 2-ketodecahydronaphthalene from cyclohexanone. C. MANNICH, W. KOCH, and F. BORKOWSKY (Ber., 1937, 70, [B], 355—359).—Gradual addition during a period of days of NaOEt in EtOH to a mixture of 2-dimethylaminomethylcyclohexanone and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ gives *Et* 10-hydroxy-3-ketodecahydronaphthalene-2-carboxylate (I), m.p. 146° (semicarbazone, m.p. 186°). (I) is transformed by NH_2OH into 11-hydroxy-3-keto-4:5:6:7:8:9:10:11-octahydronaphthhisooxazole, m.p. 183°, and by $\text{NHPh}\cdot\text{NH}_2$ into 11-hydroxy-3-keto-2-phenyl-4-11-octahydronaphthopyrazole, m.p. 183° converted by Me_2SO_4 and NaOH into 11-hydroxy-3-keto-2-phenyl-1-methyl-4-11-octahydronaphthopyrazole, m.p. 240°, and by boiling Ac_2O into 3-keto-11-acetoxy-1-acetyl-2-phenyl-4-11-octahydronaphthopyrazole, m.p. 122°, whence 3-keto-2-phenyl-4:5:6:7:8:10-hexahydronaphthopyrazole, m.p. 205°. (I) is hydrolysed by cold aq. KOH to 3-keto-1:2:3:4:6:7:8:9-octahydronaphthalene-2-carboxylic acid (II), m.p. 95° (decomp.), whence 3-keto-1:2:3:5:6:7:8:9-octahydronaphthalene, b.p. 140—141°/14 mm. (semicarbazone, m.p. 210°), which is hydrogenated (Pd-C in MeOH) to 3-ketodecahydronaphthalene (III), b.p. 120°/16 mm. (II) is reduced to 3-ketodecahydronaphthalene-2-carboxylic acid, decomp. about 90° with formation of CO_2 and (III). Treatment of 5-keto-6-dimethylaminomethyltetrahydronaphthalene and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in C_6H_6 with NaOEt-EtOH and of the product with HCl followed by distillation in a vac. gives 3-ketohexahydrophenanthrene, m.p. 80°. 2-Keto-3-methylhexahydrophenanthrene, m.p. 98—100°, is obtained analogously from $\text{CHMeAc}\cdot\text{CO}_2\text{Et}$.

H. W.

Action of phosphorus pentahalides on acetophenone. W. TAYLOR (J.C.S., 1937, 304—308).—The action of PX_5 on COPhMe is dependent on the equilibria $\text{PX}_5 \rightleftharpoons \text{PX}_3 + \text{X}_2$ and $\text{COPhMe} \rightleftharpoons \text{OH}\cdot\text{CPh}\cdot\text{CH}_2$ (II). PX_5 then acts directly on the CO and OH groups, e.g., on (I) to give CPhMeX_2 and on (II) to give $\text{CPhX}\cdot\text{CH}_2$, and X_2 adds to the double linkings, (II) thus giving $\text{COPh}\cdot\text{CH}_2\text{X}$ (III). Repeti-

tion of this mechanism gives $\text{COPh}\cdot\text{CHX}_2$ and $\text{CPhX}\cdot\text{CHX}$. With PCl_3Br_2 and (I) at 0—40° the presence of the following products is established by the methods in parentheses: (I) (as semicarbazone), $\text{COPh}\cdot\text{CH}_2\text{Br}$ (isolated, and as phenacyl succinate), $\text{CPhBr}\cdot\text{CHBr}$ (isolated), $\text{COPh}\cdot\text{CHBr}_2$ (converted into antiphenylamphiglyoxime with NH_2OH), and CPhMeBr_2 (by the kinetics of its reaction with EtOH at 55°). In agreement with the above mechanism (III) is the main product with PCl_3Br_2 (presence of more free X_2), but with PCl_5 only $\text{CPhCl}\cdot\text{CH}_2$ and CPhMeCl_2 are obtained. (I) and PBr_5 give mainly tarry material. J. W. B.

Action of organo-magnesium compounds on trialkylacetophenoneoximes. J. HOCH (Compt. rend., 1937, 204, 358—360).—Dimethyl-n-butyl- (I), m.p. 138°, and benzyl dimethyl-acetophenoneoxime (II), m.p. 191°, with excess of MgEtBr , MgPhBr , $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$, MgMeI , and MgPhBr in boiling xylene afford dimethyl-n-butyl-, b.p. 140°/17 mm., (phenyl-carbamate, m.p. 131—132°), and benzyl dimethyl-acetophenoneimine, b.p. 192—194°/18 mm. (phenyl-carbamate, m.p. 156°), respectively, hydrolysed to the ketones with warm HCl and converted into (I) and (II), respectively, with NH_2OH . MgPhBr with (I) or (II) affords $\text{CPh}_2\cdot\text{NH}$ (phenylcarbamate, m.p. 166°) as a secondary product, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ with (I) gives phenyl p-tolyl ketimine (III), b.p. 176°/13 mm. (phenylcarbamate, m.p. 167°). $\text{CPh}_2\cdot\text{NH}$ and (III) are synthesised from MgPhBr and PhCN and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CN}$, respectively. A probable mechanism for these and an analogous reaction of $\text{CPhEt}\cdot\text{N}\cdot\text{OH}$ (A., 1934, 893) are described. J. L. D.

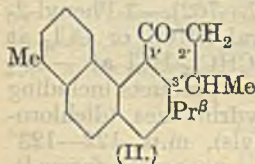
Indones. XIII. Chloro-derivatives of 3-phenyl-2-methylindone. R. DE FAZI and F. PIRONE (Gazzetta, 1936, 66, 757—762).—3-Phenyl-2-methylindone and Cl_2 in neutral CHCl_3 or CCl_4 at —10° and at 15—20°, and in $\text{CHCl}_3\text{-HCl}$ at —15°, or $\text{C}_6\text{H}_6\text{-HCl}$ at —5°, give various products including two chloro-3-phenyl-2-methylhydrindones (dichlorodiphenyldimethyldiketodi-indanyls), m.p. 122—123° and 150—151° (Cl non-reactive, no oxime formed), and three dichloro-3-phenyl-2-methylhydrindones, m.p. 85—86°, 92—93°, and 111—112° (1 Cl reactive) (cf. A., 1930, 779). E. W. W.

Configurations of α - and β -p-bromobenzophenoneoximes. R. W. JOHNSON and J. GOLENTERNEK (J. Amer. Chem. Soc., 1937, 59, 365—367).—The velocity of hydrolysis [determined essentially as previously described (A., 1934, 1180)] of α -p-bromobenzophenoneoxime (I), m.p. 168—170° (lit. 165—166°), approximates to that for $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$; the β -oxime (II), m.p. 109—111°, and 4:4'-dibromobenzophenoneoxime, m.p. 150—152°, show a similar relationship. The results suggest that (I) and (II) have the *syn*-Ph and *syn*-p- $\text{C}_6\text{H}_4\text{Br}$ configuration, respectively. H. B.

High mol. wt. aryl alkyl ketones. A. W. RALSTON and C. W. CHRISTENSEN (Ind. Eng. Chem., 1937, 29, 194—196).—The prep. and properties of the following ketones are described [recorded m.p. marked (G) refer to those made using the Grignard reactions; all others refer to compounds obtained by the Friedel-

Crafts method]: *p*-xenyl undecyl, m.p. 97—98°, (G) 97—98°, pentadecyl, m.p. 102—103°, (G) 103°, heptadecyl, m.p. 108—109°, (G) 109°; *p*-methylxenyl heptadecyl, m.p. 105—106°; *p*-chloroxenyl heptadecyl, m.p. 96—97°; phenoxyphenyl undecyl, m.p. 45—46°, (G) 46°, pentadecyl, m.p. 53·5—54·5°, heptadecyl, m.p. 68°, (G) 68°; *p*-methylphenoxyphenyl heptadecyl, m.p. (G) 77—78°, *p*-nitrophenoxyphenyl heptadecyl, m.p. 177—178°, 2-furyl undecyl, b.p. 165—166°/5 mm., (G) 167—168°/5 mm., heptadecyl, m.p. 56—57°, 5-methyl-2-furyl heptadecyl, m.p. 68—69°, 2-dibenzfuryl undecyl, m.p. 74—75°, (G) 74—75°, heptadecyl, m.p. 83—84°, (G) 83—84°, α -naphthyl undecyl, b.p. (G) 240—245°/5 mm., and heptadecyl ketone, m.p. (G) 53—54°. 2-Stearyl-, m.p. 105—106°, 2-lauryl-, m.p. 101—102°, 2:8-distearyl-, m.p. 161—162°, 2:8-dipalmityl-, m.p. 162°, 2:8-dimyristyl-, m.p. 169° and 2:8-dilauryl-carbazole, m.p. 176°; 2-lauryl-, b.p. 190—195°/4 mm., 2-myristyl-, b.p. 205—210°/4 mm., 2-stearylthiophen, m.p. 48—49° and 3-stearyldibenzothiophen, m.p. 69—70°. F. N. W.

Retene. VIII. Synthesis of 3'-methyl-5:6-cyclopentenoretene [1:3'-dimethyl-7-isopropyl-5:6-cyclopentenophenanthrene]. D. E. ADELSON and M. T. BOGERT (J. Amer. Chem. Soc., 1937, 59, 399—401).—6-Acetylretene (I), $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Zn dust in C_6H_6 + I give, after hydrolysis ($\text{MeOH}\cdot\text{KOH}$), β -hydroxy- β -6-retylbutyric [β -hydroxy- β -1-methyl-7-isopropyl-6-phenanthrylbutyric] acid, m.p. 121—122° [*Me* ester, m.p. 90—90·5°, from (I) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Me}$], dehydrated (boiling Ac_2O + NaOAc) to β -6-retylcrotonic acid, m.p. 205—206° (decomp.), which is reduced (3% Na-Hg, $\text{MeOH}\cdot\text{KOH}$) to β -6-retylbutyric acid, m.p. 152·5—153·5°. The chloride of this with AlCl_3 in C_6H_6 gives 1'-keto-3'-methyl-5:6-cyclopentenoretene (II), m.p. 111·5—112·5° [oxime, m.p. 194—195° (decomp.)], which is reduced (Clemmensen) to 3'-methyl-5:6-cyclopentenoretene, m.p. 74·5—75·5° (unstable picrate, m.p. 154—155°). All m.p. are corr.

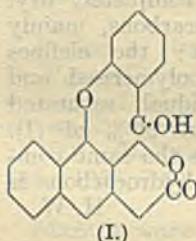


Benzanthrone and 4-phenylbenzanthrone. C. F. H. ALLEN and S. C. OVERBAUGH (J. Amer. Chem. Soc., 1937, 59, 423).—Priority claimed by Carrier and Ghigi (A., 1936, 1511) is acknowledged.

Oxidative demolition of 6-phenylmeso-benzanthrone with an alkaline solution of potassium permanganate. G. CHARRIER and (SIGNA.) E. GHIGI (Atti R. Accad. Lincei, 1936, [vi], 24, 72—77).—In the oxidation of 6-phenylmeso-benzanthrone by $\text{KMnO}_4\text{--NaOH}$ (cf. A., 1935, 751), 4-phenylantraquinone-1-carboxylic acid (I) is considered to be a by-product, and the main product to be 3:4-dicarboxydiphenyl-2-glyoxylic acid (II), m.p. 256—257° (decomp.). Prolonged oxidation of (II) by $\text{KMnO}_4\text{--NaOH}$ gives (I); $\text{KMnO}_4\text{--H}_2\text{SO}_4$ oxidises (II) to diphenyl-2:3:4-tricarboxylic acid (III), m.p. 210—212°. Either (II) or (III) with conc. H_2SO_4 yields fluorenone-1:2-dicarboxylic acid (IV), m.p. 330° [*Me* ester, m.p. 230° (decomp.); *Me*₂ ester, m.p. 199°].

The *Me* ester above its m.p., or (IV) with Ac_2O , gives the anhydride, m.p. 315—320°. (IV) is decarboxylated to fluorenone-2-carboxylic acid, m.p. 330° (*Me* ester, m.p. 186°). With $\text{NHPh}\cdot\text{NH}_2$, (IV) gives its phenylhydrazone, m.p. 305—307° (anhydride, m.p. 315°), and fluorenone-1:2-dicarboxyanilinoimide phenylhydrazone, m.p. 276°. E. W. W.

Oxidative demolition of 6-phenylmeso-benzanthrone with an acetic acid solution of chromic anhydride. G. CHARRIER and (SIGNA.) E. GHIGI (Atti R. Accad. Lincei, 1936, [vi], 24, 65—72).—6-Phenylmeso-benzanthrone with $\text{CrO}_3\text{--AcOH}$ gives a CrO_2 -complex, oxidised to the cyclol (I), m.p. 296—305° (decomp.), of 1:2:3:4-dibenzoxanthone-2'-carboxylic acid (not isolated in ketonic form) (*Na* salt, +3 H_2O ; *Me* ester, m.p. 217°). (I) is converted by boiling 20% *NaOH* into 9-o-hydroxybenzoylfluorene-1:9-dicarboxylic acid, m.p. 210—212°. (I) is oxidised by $\text{KMnO}_4\text{--NaOH}$ to diphenyl-2:3:2'-tri-



carboxylic acid [also obtained from benzanthrone; converted by H_2SO_4 into fluorenone-1:5-dicarboxylic acid, m.p. 295—299° (*Me*₂ ester, m.p. 120°)], and salicylic acid. Distillation of (I) over hot Zn (which gives also phenanthrene), or, better, heating of (I) with quinoline and Cu, yields 1:2:3:4-dibenzoxanthone, m.p. 209°, oxidised by KMnO_4 to diphenic acid, and converted by $\text{KOH}\text{--EtOH}$ (pressure) into o-hydroxyphenyl 9-hydroxy-10-phenanthryl ketone, and by KOH fusion into salicylic acid and 9-hydroxyphenanthrene. E. W. W.

Chloro- and fluoro-compounds related to adrenalone. H. L. HANSEN (J. Amer. Chem. Soc., 1937, 59, 280—281).—o-Chlorophenyl chloroacetate, b.p. 123—125°/6 mm. [prepared from o- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, and SOCl_2 by the method of Hartung *et al.* (A., 1932, 157)], with AlCl_3 in CS_2 gives ω :3-dichloro-4-hydroxyacetophenone, m.p. 141—142°, which with NH_2Me in aq. EtOH affords 3-chloro- ω -methylamino-4-hydroxyacetophenone (I) (hydrochloride, shrinks at 180°, melts partly at 210—211°, and decomp. 217°). The *Me* ether of (I) is oxidised (KMnO_4) to 4:3- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$ o-Fluorophenyl chloroacetate, b.p. 90—94°/4 mm., m.p. 36—38°, similarly yields ω -chloro-, m.p. 101—102°, and thence ω -methylamino- (II) [hydrochloride, m.p. 235—236° (decomp.) (darkens at 228°)] 3-fluoro-4-hydroxyacetophenone. 4:3- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{F}\cdot\text{CO}_2\text{H}$, m.p. 208—210° (lit. 204°), is prepared by oxidation of the *Me* ether of (II) and of 3:1:4- $\text{C}_6\text{H}_3\text{FMe}\cdot\text{OMe}$. (I) and (II) possess weak vaso-pressor properties. H. B.

Amide condensations. Benzoylacetone from acetdiphenylamide and acetophenone. G. TSCHELINCEV and E. OSETOVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 419—421).— NPh_2Ac with Na and COPhMe in C_6H_6 gives $\text{CHAc}\cdot\text{CPh}\cdot\text{ONa}$, which with acid gives CH_2BzAc in 25% yield. NEt_2Ac does not react in this way. A. Li.

Action of organometallic compounds on α -oxido-ketones. C. L. BICKEL (J. Amer. Chem.

Soc., 1937, 59, 325—328).—The diol obtained from α -anisoyl- β -phenylethylene oxide (I) and $\text{Et}_2\text{O-MgPhBr}$ (1 equiv. at -15° or 4 equivs. at room temp.) is $\alpha\beta$ -dihydroxy- $\alpha\gamma\gamma$ -triphenyl- α -anisylpropane (II), m.p. 132° (cf. Bergmann and Wolff, A., 1932, 616), since it is oxidised (CrO_3 , AcOH) to COPh_2 and *p*-methoxybenzophenone (III), and differs from $\alpha\gamma$ -dihydroxy- $\alpha\gamma\gamma$ -triphenyl- α -anisylpropane (IV), m.p. 150° . The anisyl group may promote fission of the oxide ring (cf. Kohler *et al.*, A., 1931, 354). (I) and $\text{Et}_2\text{O-LiPh}$ at -15° give $\beta\gamma$ -oxido- $\alpha\gamma$ -diphenyl- α -anisylpropyl alcohol (V), m.p. 136° ; at room temp. fission of (V) occurs. (V) is converted by boiling $\text{Et}_2\text{O-LiPh}$ into *p*-methoxytriphenylcarbinol, by MgPhBr into (II), and is rearranged by MeOH-KOH into the unstable $\beta\gamma$ -oxido- $\alpha\gamma$ -diphenyl- γ -anisylpropyl alcohol (VI), m.p. about 120° , which undergoes ready autoxidation to α -hydroxybenzyl $\alpha\beta$ -oxido- β -phenyl- β -anisylethyl peroxide (VII), m.p. 150° (decomp.). (V), (VI), and (VII) are all oxidised (CrO_3) to BzOH and (III). α -Benzoyl- β -phenyl- and β -*o*-chlorophenylethylene oxides with $\text{Et}_2\text{O-LiPh}$ at -15° similarly give $\beta\gamma$ -oxido- $\alpha\gamma$ -triphenyl- and $\alpha\alpha$ -diphenyl- γ -*o*-chlorophenyl-propyl alcohol, respectively. *p*-Methoxydibenzoylmethane and $\text{Et}_2\text{O-MgPhBr}$ (4 equivs.) afford β -benzoyl- α -phenyl- α -anisylethyl alcohol, m.p. 132° [oxidised (CrO_3 , AcOH) to BzOH and (III)], and β -anisoyl- $\alpha\alpha$ -diphenylethyl alcohol, m.p. 118° (oxidised to COPh_2 and anisic acid), both of which are converted by $\text{Et}_2\text{O-LiPh}$ at 0° into (IV). H. B.

Dioximes. CXVII. P. GRAMATIERI (Gazzetta, 1936, 66, 753—757).—"Oximinobenzoyldimethylglyoxime peroxide" (A., 1904, i, 428), renamed as the oxime of phenylethyltriketone-1:3-dioxime peroxide (cf. A., 1936, 1383) is converted by $\text{NH}_2\text{OH.HCl}$ in $\text{C}_5\text{H}_5\text{N}$ into phenylethyltriketonetrioxime, m.p. 185° (decomp.) [Ac_3 , m.p. 115 — 116° , and Bz_3 , m.p. 96 — 97° , derivatives; $\text{C}_5\text{H}_5\text{N}$, m.p. 171 — 172° (decomp.), and NHPPh.NH_2 , m.p. 171° (decomp.), salts]. Ethylbenzylidenemethylketoxime, unlike benzylidenemethylketoxime, is decomposed by HNO_3 to form p - $\text{NO}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$. E. W. W.

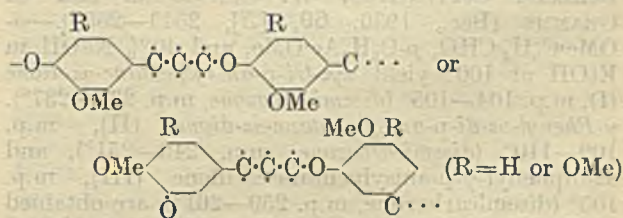
Dioximes. CXIX. G. PONZIO and M. FORMASERI. CXX. G. LONGO. CXXI. G. PONZIO (Gazzetta, 1936, 66, 812—815, 815—819, 819—826).—CXIX. $\alpha\epsilon$ -Diketo- $\alpha\epsilon$ -diphenyl-*n*-pentanedioxime (Auger, Ann. Chim., 1891, [vi], 22, 358) exists in a single form (I), m.p. 165 — 166° (decomp.) (Ac_2 , m.p. 69 — 70° , and Bz_2 , m.p. 179 — 180° , derivatives), converted by N_2O_4 into $\alpha\alpha\epsilon\epsilon$ -tetranitro- $\alpha\epsilon$ -diphenylpentane, m.p. 98 — 99° , by NaOH-NaOCl into $\alpha\epsilon$ -diketo- $\alpha\epsilon$ -diphenyl-*n*-pentaneoxime, m.p. 11 — 12° , and by POCl_3 into glutardianilide. The compounds, m.p. 151° and 161° , previously reported, are impure (I); the compound, m.p. 62° (A., 1899, i, 60), is derived from some impurity in the $\text{CH}_2(\text{CH}_2\text{Bz})_2$ used.

CXX. CHPh:CH-CPh:N-OH with AcOH-NaNO_2 gives diphenyltriketonetrioxime $\alpha\gamma$ -peroxide, $\text{CPh} \begin{smallmatrix} \text{C(N-OH)} \\ \text{N-O-N} \end{smallmatrix} \text{CPh}$, m.p. 208° (decomp.), with diphenyltriketone- $\alpha\gamma$ -dioxime peroxide, m.p. 194° (decomp.) [also obtained from $\text{CO}(\text{CH}_2\text{Ph})_2$ and HNO_2]; structures of similar compounds (A., 1936, 1383) are

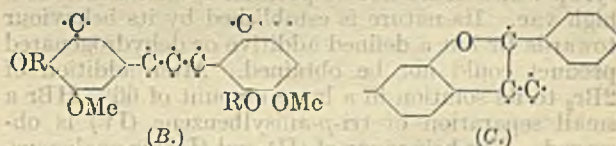
thus confirmed. Either product with NH_2OH yields diphenyltriketonetrioxime.

CXXI. β -Benzoylmethylglyoxime peroxide (4-benzoyl-3-methyl-1:2:5-oxadiazole 5-oxide) (II) with $\text{NH}_2\text{OH.HCl}$ gives its β -oxime (III), m.p. 129 — 130° (Ac, m.p. 117 — 118° , and Bz, m.p. 157 — 158° , derivatives), which with POCl_3 yields methylglyoximecarboxylanilide peroxide, m.p. 150 — 151° , and with 20% NaOH , the Na salt of the nitronic acid corresponding with α -nitromethylbenzylloxadiazole (Br derivative). With N_2O_4 , (III) gives " β "-methyl- $\alpha\alpha$ -dinitrobenzylglyoxime peroxide (IV), m.p. 100 — 101° (decomp.). (IV) is converted by NHPPh.NH_2 into the β -phenylhydrazone, m.p. 225° (decomp.), of (II). $\text{SnCl}_2\text{-AcOH}$ reduction of (IV) gives (II), which with NHPPh.NH_2 yields the α -phenylhydrazone, m.p. 125° , with some of the β -form, into which it is converted by heating above its m.p., or by boiling 20% HCl . The structure and reactions of (III) are discussed. E. W. W.

Model experiments related to the fission of lignin. I. Fission of propenylpyrocatechol ethers by sodium alkoxide. A. VON WACEK and I. MORGHEN. II. Action of sodium hydroxide and sodium ethoxide on substituted chalcones and dehydrodiisoeugenol methyl ether. A. VON WACEK and E. DAVID (Ber., 1937, 70, [B], 183—189, 190—195).—I. Three possible modes of union of a simple component such as coniferyl alcohol to a polymeric lignin are discussed. The simplest is continuous direct etherification of one component with the next thus,



(type A). Alternatively a C-C linking may be developed during polymerisation thus leading to type B or a combination of these modes of union may



take place giving type C. Propenylpyrocatechol ethers are selected as representative of type A and the reaction is quantitatively studied by use of solubility relationships in a ternary system. With isoeugenol Me ether elimination of the two Me occurs nearly to the same extent; the *p*-Me is somewhat the more mobile, the approx. ratio being 47:53. The size of the radical is very significant. The ratio of eliminated Et to eliminated Me is about 20—80 when Et is in position 4 and Me in position 3 to the side-chain. The influence of position is noticeable since the ratio becomes about 10:90 when the relative positions are reversed. The effect of medium (NaOMe in MeOH or NaOEt in EtOH) is very small and the effect of temp. between 150° and 180° is only about

5%. The ratio of the products of fission does not depend on the duration of the experiment. Reaction appears to be bimol.

II. As representative of type B, 3':4':4'-trimethoxychalkone (I) is treated with boiling 33% KOH whereby unchanged material and *anisylidenedi-3:4-dimethoxyacetophenone*, m.p. 160.5—161° [obtained also from *p*-OMe·C₆H₄·CHO and 3:4-C₆H₃Ac(OMe₂)], are isolated. 3':4'-Dimethoxychalkone (II) gives *benzylidenedi-3:4-dimethoxyacetophenone*, m.p. 147.5—148° (identified by conversion into 4-phenyl-2:6-di-3':4'-dimethoxyphenylpyridine), and *dibenzylidenetri-3:4-dimethoxyacetophenone*, m.p. 220°. 4-Hydroxy-3':4'-dimethoxy- and 4'-hydroxy-3:4-dimethoxychalkone are transformed by protracted boiling with 15% KOH into the corresponding acetophenones and aldehydes; defined higher condensation products are obtained in small amount or not at all. Independently of the presence of free OH, the action of NaOEt under pressure follows a different course leading in the cases of (I) and (II) to marked loss of OMe. Ethylation of the products and subsequent oxidation gives only *p*-OEt·C₆H₄·CO₂H in small amount. As representative of type C, dehydrodiisoeugenol Me ether loses much OMe when treated with NaOEt under pressure but methylation of the product leads to the original material so that no marked change occurs in the skeleton.

H. W.

Grignard reaction with aryl-substituted α -diketones and its application to the syntheses of benzene derivatives. W. SCHNEIDER and G. GRAMMS (Ber., 1936, 69, [B], 2543—2557).—*p*-OMe·C₆H₄·CHO, *p*-C₆H₄Ac·OMe, and 40% NaOH in EtOH at 100° yield $\alpha\gamma$ -tri-*p*-anisylpentane- α -dione (I), m.p. 104—105° (*disemicarbazone*, m.p. 235—237°). γ -Phenyl- α -di-*p*-anisylpentane- α -dione (II), m.p. 109—110° (*disemicarbazone*, m.p. 249—251°), and $\alpha\alpha$ -diphenyl- γ -*p*-anisylpentane- α -dione (III), m.p. 105° (*disemicarbazone*, m.p. 259—261°), are obtained similarly. Rapid addition of (I) in PhOMe to MgMeI (2 mols. in Et₂O) gives $\beta\delta\zeta$ -tri-*p*-anisyl- Δ^8 -heptadiene, which could be obtained only as a yellow to brown syrup which could not be purified by distillation in a high vac. Its nature is established by its behaviour towards Br but a defined additive or dehydrogenated product could not be obtained. After addition of 2Br₂ to its solution in a large amount of 66% HBr a small separation of tri-*p*-anisylbenzene (IV) is observed. The behaviour of (II) and (III) is analogous. Addition of MgMeI in Et₂O to a well-cooled solution of (I) in PhOMe gives an immediate gelatinous ppt. which regenerates (I) on addition of dil. H₂SO₄; if 2 mols. of the reagent are used and the mixture is preserved the amorphous ppt. slowly becomes cryst. and when decomposed yields $\alpha\gamma$ -tri-*p*-anisyl- Δ^8 -hexen- α -one (V), m.p. 166—167° (*sulphate*). γ -Phenyl- α -tri-*p*-anisyl- Δ^8 -hexen- α -one, m.p. 173°, $\alpha\alpha$ -diphenyl- γ -*p*-anisyl- Δ^8 -hexen- α -one, m.p. 180°, and $\alpha\gamma$ -triphenyl- Δ^8 -hexen- α -one, m.p. 139°, are obtained similarly. Titration of (V) in AcOH-66% HBr with Br and decomp. of the product with H₂O gives (IV), m.p. 142—143°. 1-Phenyl-3:5-di-*p*-anisylbenzene, m.p. 135°, 1:5-diphenyl-3-*p*-anisylbenzene, m.p. 139°, and *s*-C₆H₃Ph₃ are analogously derived. (I) and MgEtI

afford $\alpha\gamma$ -tri-*p*-anisyl- Δ^8 -hepten- α -one, m.p. 139°, whence 2:4:6-tri-*p*-anisyltoluene, m.p. 127—128°.

H. W.

Direct transformation of 2:2'-di-indandionyl into dihydroxynaphthacenequinone. G. WANAG [with A. LODÉ] (Ber., 1937, 70, [B], 274—277).—2:2'-Di-indandionyl is partly isomerised to dihydroxynaphthacenequinone when boiled under reflux with 0.5*N*-NH₃; poorer yields are obtained with a more conc. reagent. A similar change occurs with boiling 10% NaOAc or C₂H₅N but not with aq. NaOH probably owing to the formation of a stable Na derivative.

H. W.

Retene and dihydroretene. G. A. NYMAN (Ann. Acad. Sci. fenn., 1935, 41, No. 5, 74 pp.; Chem. Zentr., 1936, i, 2348—2350).—Dihydroretene (I) with a slight excess of AcCl and AlCl₃ in CS₂ yields β -acetyldihydroretene (II), m.p. 77° (*oxime*, m.p. 174—175°; *semicarbazone*, m.p. 256—257°; *phenylhydrazine*, m.p. 139—141°; *benzylidene derivative*, m.p. 105—106°), oxidised (CrO₃-AcOH) to β -acetylretenequinone, m.p. 193—194°; these are shown to be different from the α -acetylretene derivatives of Bogert and Hasselström (A., 1931, 1297). (I) with excess of AcCl and AlCl₃ in CS₂ yields diacetyldihydroretene (III), m.p. 147—148° (*dioxime*, m.p. 194—195°), oxidised to diacetylretenequinone, m.p. 205—207°. NaOBr oxidation of (II) yields dihydroretene- β -carboxylic acid (IV), m.p. 228.5—230° (*Me ester*, m.p. 85—86°; *amide*, m.p. 247—248°; *anilide*, m.p. 229—230°), oxidised (CrO₃-AcOH) to retenequinone- β -carboxylic acid, m.p. 249—250° (decomp.) (*Me ester*, m.p. 217—218°). (III) is oxidised (NaOBr) to dihydroretene-dicarboxylic acid (V), m.p. 275.5—276.5° (*diamide*, m.p. 289—291°), which with Ac₂O yields a substance, C₁₈H₁₈(CO₂H)·CO₂Ac (?), m.p. 95—109°, which with NH₂Ph affords the *anilic acid* of (IV), m.p. 249.5—253°. (V) is also obtained from (I) and (COCl)₂ with AlCl₃. (IV) is reduced (Na-C₅H₁₁-OH) to a mixture of hexahydroretene- β -carboxylic acid I, m.p. 201.5—203° (*Na salt*; *Me ester*, m.p. 73—75°), and hexahydroretene- β -carboxylic acid II, m.p. 154—156° (*Na salt*; *Me ester*, m.p. 63—64°). Similar reduction of retene- α -carboxylic acid yields a mixture of octahydroretene- α -carboxylic acid, m.p. 186—187.5°, hexahydroretene- α -carboxylic acid, m.p. 147.5—149.5° (*Na salt*), and a substance, m.p. 126—131°. Reduction (Clemmensen and Wolff-Kishner) of (II) yields β -ethylidihydroretene, m.p. 51—52.5°, oxidised to β -ethylretenequinone, m.p. 197—199°. Diethyldihydroretene, b.p. 238—241°/9 mm., and diethylretenequinone, m.p. 176—178°, are similarly obtained from (III). Retene and Pr²Br in CS₂ with AlCl₃ yield an isopropylretene (VI), b.p. 231—233°/9.5 mm. (*picrate*, m.p. 154.5—155.5°; *stypnate*, m.p. 117.5—118.5°), oxidised to an isopropylretenequinone, m.p. 162.5—163.5°. α -Acetylretene and MgMeI yield α -isopropenylretene, m.p. 64.5—65.5° (*picrate*, m.p. 136—137°), hydrogenated to α -isopropylretene, m.p. 52—53° (*picrate*, m.p. 160.5—161.5°), not identical with (VI).

H. N. R.

Hydroxyanthraquinones. II. 1:2:5:6- and 1:4:5:8-Tetrahydroxyanthraquinones. P. G. MARSHALL (J.C.S., 1937, 254—255).—Fusion of

anthrarufindisulphonic acid (improved prep.) with NaOH-NaClO₃ at 260–270° gives a 70–75% yield of 1:2:5:6-tetrahydroxyanthraquinone [*Ac*₄ derivative, m.p. 260–275° (decomp.)], converted by 20% oleum at 120–130° into a (SO₃H)₂ derivative, from which a (OH)₆-compound could not be obtained. 1:4:5:8-Tetrahydroxyanthraquinone, m.p. >300° [*Ac*₄ derivative, m.p. >258° (decomp.)], is obtained by boiling its leuco-compound, m.p. >290° (decomp.) [*Ac* derivative, m.p. 235–240° (decomp.)] (by boiling diaminoanthrarufin with NaOH-Na₂S₂O₄), with PhNO₂. J. W. B.

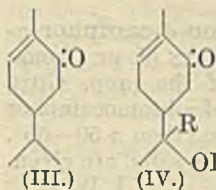
Demolition of isodibenzanthrone (isoviolanthrone) by oxidation with an alkaline solution of potassium permanganate. (SIGNA.) E. GHIGI (Atti R. Accad. Lincei, 1936, [vi], 24, 78–82).—This oxidation yields anthraquinone-1:2-dicarboxylic acid, 3:2-dicarboxydiphenyl-2-glyoxylic acid, and phthalic acid. isodibenzanthrone thus behaves as two linked benzanthrone nuclei, and not as a perylene derivative. E. W. W.

Menthone series. XIV. *dl*-1-Hydroxymenthone, *dl*-menthane-1:3-diols, and *dl*-Δ⁶-neomenthen-3-ol. J. READ and G. SWANN (J.C.S., 1937, 237–238).—*dl*-1-Hydroxymenthone, prepared by catalytic hydrogenation of *dl*-piperitone oxide, with semicarbazide acetate gives the semicarbazide, m.p. 190–190.5°, of *dl*-piperitone (p-nitrobenzoate, m.p. 109°) and is hydrogenated to a mixture of diols, b.p. 129–138°/12.5 mm. (monoacetate, b.p. 130–136°/17 mm.), from which *dl*-menthane-1:3-diol, m.p. 143° [3:5-dinitrobenzoate, m.p. 199–200° (decomp.)], can be separated. Dehydration (KHSO₄) of the diols yields *dl*-Δ⁶-neomenthen-3-ol, b.p. 99°/17.5 mm. (3:5-dinitrobenzoate, m.p. 118–119°), partly oxidised (Beckmann's reagent) to a substance, b.p. 93–95°/17 mm. (semicarbazone, m.p. 179–180°), and resisting dehydration to α-phellandrene. F. R. S.

Carvone series. IV. Optically active carvotanacetols and carvotanacetylaminines. J. READ and G. SWANN (J.C.S., 1937, 239–242).—Reduction [Pr^βOH and Al(OPr^β)₃] of *d*-carvotanacetone gives a mixture from which has been isolated *d*-carvotanacetol, b.p. 101°/13 mm., α_D²⁰ +100.5° (p-nitrobenzoate, m.p. 93.5–94°, [α]_D²⁰ +85.0°), and products converted into carvotanacetyl p-nitrobenzoate, m.p. 60–62°, [α]_D²⁰ –51.3°, and 3:5-dinitrobenzoate, m.p. 88.5–90°, [α]_D²⁰ –33.3°. The *d*-carvotanacetol undergoes partial racemisation in presence of acids, owing probably to anion migration or to successive hydration and dehydration. *d*-Carvotanacetone (I) is reduced (Zn-AcOH) to *d*-carvotanacetylamine, b.p. 93°/16.5 mm., [α]_D²⁰ +190.1° (*H* d-tartrate, m.p. 141–142°, [α]_D²⁰ +95.5° in H₂O; *H* oxalate, m.p. 205°, [α]_D²⁰ +102.3° in H₂O; *Ac* derivative, m.p. 112°, [α]_D²⁰ +155.3° in CHCl₃; *Bz* derivative, m.p. 97–98°, [α]_D²⁰ +214.0° in CHCl₃; stereoisomeric *Bz* derivative, m.p. 165°, [α]_D²⁰ –87.5° in CHCl₃). The mechanism postulated (cf. A., 1934, 528) for the production of piperitylamine from piperitone has been confirmed by similar studies of the reaction between (I) and N₂H₄. F. R. S.

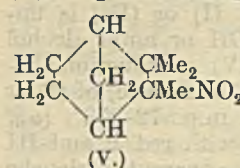
Addition of alcohols at double linkings. I. Addition of alcohols to carvone and dihydro-

carvone. W. TREIBS (Ber., 1937, 70, [B], 384–388).—In the presence of moderate amounts of mineral acid, 2 mols. of an aliphatic alcohol are added to 1 mol. of carvone (I) or dihydrocarvone (II) giving products in which only one Oalk is present. Since addition does not occur with carvotanacetone (III), union is with the aliphatic double linking giving products such as (IV) and is probably preceded by the transformation of the alcohol into the corresponding ether. (I) is transformed by prolonged boiling with 8–10% H₂SO₄-MeOH into the substance



(V), C₁₂H₂₀O₂, b.p. 130–131°/17 mm., α_D²⁰ +40.5° (semicarbazone, m.p. 139°), converted by H₂O₂ and KOH in MeOH into the oxide (IV), C₁₂H₂₀O₃, b.p. 132–134°/17 mm., α_D²⁰ –19.5°. Similarly (II) affords the compound, C₁₂H₂₂O₂, b.p. 118–120°/17 mm., α_D²⁰ –20.8° (semicarbazone, m.p. 142°), also obtained by hydrogenation (colloidal Pd in MeOH) of (V). (I) and EtOH give the product, C₁₄H₂₄O₂, b.p. 134–135°/17 mm., α_D²⁰ +38°, transformed into the corresponding oxide (VII), b.p. 133–135°/17 mm., α_D²⁰ –19°. Treatment of carvone oxide, (VI), or (VII) with AcOH-conc. HCl at 100° affords dehydrocarvacrol, (C₁₀H₁₂O)₂, m.p. 180°. With more conc. H₂SO₄ in the requisite alcohol at 100° (I) yields carvacryl Me, Et, and Buⁿ ether, b.p. 98°/17 mm., 105°/17 mm., and 120–121°/17 mm., respectively. H. W.

Change of molecular structure during chemical reactions. III. Reaction of bornylamine and isobornylamine with nitrous acid. W. HÜCKEL and F. NERDEL (Annalen, 1937, 528, 57–73; cf. A., 1933, 372).—*iso*Bornylamine (modified prep.) and HNO₂ give only pure camphene (I) and camphene hydrate (II). Bornylamine (modified prep.) and HNO₂ give much pure (I) and (II) with some *d*-α-terpineol (III), m.p. 39–40°, [α]_D²⁰ +42.88° [dibromide, m.p. 122°; p-nitrobenzoate (IV), m.p. 139°; nitrosochloride, m.p. 125° (decomp.); nitropiperidine, m.p. 150°; with HI gives *dl*-trans-limonene dihydride, m.p. 77–78°], and traces of isomeric tert.-alcohols (p-nitrobenzoates, m.p. 129° and 108°, [α]_D²⁰ –15.1° and +12.1° in CHCl₃, respectively), and nitroisocamphene (V), m.p. 198°, [α]_D²⁰ +32.2° in EtOH. Hydrogen-



ation (PtO₂; HCl-EtOH) of (IV) gives the aminobenzoate of *dl*-dihydro-α-terpineol (p-nitrobenzoate, m.p. 96–97°), which with CrO₃ gives 4-methylcyclohexanone (semicarbazone, m.p. 196–197°; oxime p-nitrobenzoate, m.p. 104°) and β-methyladipic acid. (IV) and CrO₃ give ε-keto-β-α'-hydroxyisopropylheptioic acid p-nitrobenzoate, m.p. 101–102°. Oxidation of crude (III) successively by CrO₃ and KMnO₄ proceeds as described by Wallach, but gives also hydroxymenthane-tricarboxylic acid, m.p. 115° (decomp.). (V) is reduced with difficulty to *d*-aminocamphane (*Bz* derivative, m.p. 146°, [α]_D²⁰ –9.3° in CHCl₃), and by Al-Hg in moist Et₂O to an oily *NO*-compound. (V) is also obtained ([α]_D²⁰ –10° in CHCl₃) from *d*-camphene by treating the hydrochloride with AgNO₂ and reducing

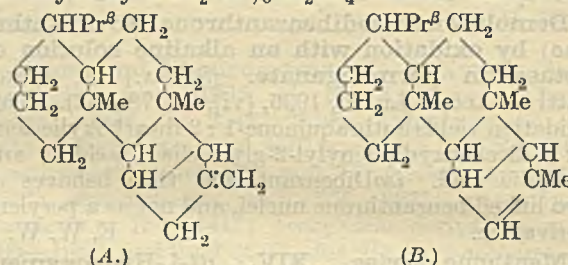
the mixed NO_2 - and $\text{O}\cdot\text{NO}$ -compound by $\text{Na}\cdot\text{EtOH}$. Crude *l*-camphene gives benzamidocamphanes with m.p. 146° and 125° . Only alcohols having a $\text{CMe}_2\cdot\text{OH}$ in this series give *p*-nitrobenzoates. *l*-Camphene, $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, and $o\text{-C}_6\text{H}_4(\text{CO}_2)_2\text{O}$ at 140° give a little *dl*-isobornyl phthalate, m.p. 145° . R. S. C.

Preparation of pure α -bromo-*d*-camphor- π -sulphonate. H. REGLER and F. HEIN (J. pr. Chem., 1937, [ii], 148, 1—4).—Details of the prep. (70% yield) of this acid by sulphonation of α -bromocamphor with $\text{H}_2\text{SO}_4\text{-SO}_3$ (*d* 1.865) at $<18^\circ$ and then $>50\text{--}55^\circ$, and isolation through its NH_4 and Ag salts, are given. J. W. B.

Oxypinocamphone, a new terpene ketol. T. KUWATA (J. Soc. Chem. Ind. Japan, 1937, 40, 11—12B; cf. this vol., 67).—*i*-1-Hydroxy-6-keto-1:3:3-trimethyl-2:4-methylenecyclohexane, m.p. $38.5\text{--}39.5^\circ$ [semicarbazone, m.p. $213\text{--}214^\circ$ (decomp.); acetate, b.p. $104\text{--}108^\circ/4\text{ mm.}$], with $\text{H}_2\text{C}_2\text{O}_4$ in COMe_2 affords carvacrol and a ketone, b.p. $204\text{--}212^\circ$ (oxime, m.p. $103\text{--}104.5^\circ$; semicarbazone, m.p. $154\text{--}155^\circ$). J. D. R.

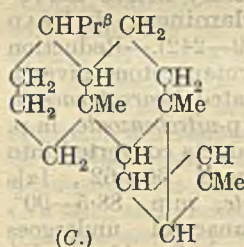
Sciadopitene, a new, crystalline diterpene, from the oil of the leaves and twigs of *Sciadopitys verticillata*, S. et Z. H. UOTA (J. Dept. Agric. Kyushu Imp. Univ. Japan, 1937, 5, 117—193).—Distillation of the material with steam and fractional distillation of the resulting oil under diminished pressure gives *sciadopitene* (I), m.p. $95\text{--}96^\circ$, $[\alpha]_D^{20} +11.05^\circ$ in CHCl_3 (yield about 5% of the oil). It contains 1 double linking. It yields a *nitrosochloride*, m.p. $127\text{--}128^\circ$ (decomp.), *nitrosate*, m.p. $126\text{--}127^\circ$ (decomp.), *nitrosite*, m.p. $132\text{--}133^\circ$ (decomp.), *di-bromide*, m.p. $122\text{--}123^\circ$, $[\alpha]_D^{20} +9.34^\circ$ in CHCl_3 , *monohydrochloride* (II), m.p. 106° after softening at 101° , $[\alpha]_D^{20} +7.77^\circ$ in C_6H_6 , and *monohydrobromide* (III), m.p. $141\text{--}142^\circ$ (decomp.), $[\alpha]_D^{20} +8.06^\circ$ in CHCl_3 . (II) with KOAc in boiling EtOH or with NH_2Ph at 100° affords *isosciadopitene* (IV), m.p. $110\text{--}111^\circ$, $[\alpha]_D^{20} +22.13^\circ$ in CHCl_3 , also obtained from (I) and H_2SO_4 in boiling EtOH or HCO_2H at $120\text{--}125^\circ$ but not with boiling AcOH . (IV) does not give a cryst. *nitrosochloride*, *nitrosate*, or *nitrosite*, affords a *di-bromide*, m.p. $133\text{--}134^\circ$ (decomp.), $[\alpha]_D^{20} +10.57^\circ$ in CHCl_3 , is converted by HCl in well-cooled, anhyd. Et_2O into (II) from which it is regenerated by $\text{KOAc}\cdot\text{EtOH}$ and by HBr into (III). (I) or (IV) is unaffected by Na and boiling EtOH or amyl alcohol whereas (II) is converted into (IV). Reduction ($\text{Pt}\cdot\text{black}$ in EtOAc or AcOH ; $\text{Pd}\cdot\text{C}$ in EtOAc) of (I) or (IV) affords *dihydrosciadopitene*, m.p. $72\text{--}73^\circ$, $[\alpha]_D^{20} +22.87^\circ$ in CHCl_3 . (I) or (IV) with red P and HI (*d* 1.7) at 150° or 250° affords the apparently tricyclic *hydrocarbon*, $\text{C}_{20}\text{H}_{36}$, b.p. $175\text{--}176^\circ/6\text{ mm.}$, $[\alpha]_D^{20} +10.59^\circ$ in CHCl_3 . Dehydrogenation of (I) or (IV) by Se at $330\text{--}350^\circ$ gives *scianthrene* (V), $\text{C}_{18}\text{H}_{18}$, m.p. $86\text{--}87^\circ$ (*picrate*, m.p. $123\text{--}124^\circ$; *styphnale*, m.p. $138\text{--}139^\circ$; *trinitrobenzoate*, m.p. $146\text{--}147^\circ$), regarded as a phenanthrene derivative not substituted at C_9 or C_{10} , since it is oxidised to *scianthrenequinone* (VI), m.p. $183\text{--}184^\circ$ (*quinoxaline* derivative, $\text{C}_{24}\text{H}_{20}\text{N}_2$, m.p. 146°). During hydrogenation, therefore, (I) or (IV) loses 2 C united to *tert.* C atoms. Oxidation of (V) by $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution yields phen-

anthrene-1:7-dicarboxylic acid; the Me_2 ester, m.p. $150\text{--}151^\circ$, is oxidised by CrO_3 in AcOH to the corresponding *quinone*, $\text{C}_{18}\text{H}_{12}\text{O}_6$, m.p. $223\text{--}224^\circ$ (decomp.). Oxidation of (VI) with KMnO_4 in $\text{C}_2\text{H}_5\text{N}\cdot\text{H}_2\text{O}$ and of the product with HNO_3 gives *diphenyl-2:3:2':4'-tetracarboxylic acid* (Me_4 ester, m.p. $151\text{--}152^\circ$), 1:2:3- and 1:2:4- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$, establishing the presence of a 7-methyl-1-isopropyl-hydrophenanthrene skeleton in (I). (I) is oxidised by boiling HNO_3 (*d* 1.18) to a substance, $\text{C}_{20}\text{H}_{32}(\text{NO}_2)_2$, and appears to be either unattacked or completely destroyed by MnO_2 —57% H_2SO_4 — AcOH . Mild treat-



ment of (I) with KMnO_4 (= 3 O) in COMe_2 at 0° gives *sciadopitene glycol*, m.p. $172\text{--}173^\circ$ (*diacetate*, m.p. 134°), which does not react with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ and a *ketone* (VII), $\text{C}_{19}\text{H}_{30}\text{O}$, m.p. $100\text{--}101^\circ$ [*semicarbazone*, m.p. $230\text{--}231^\circ$ (decomp.)], in which CO is present in the ring since it is not attacked by NaOBr ; more drastic treatment (KMnO_4 =9 O) leads to the *dicarboxylic acid* (VIII), $\text{C}_{19}\text{H}_{30}\text{O}_4$, m.p. $202\text{--}203^\circ$ (decomp.). Similar mild treatment of (IV) gives the *CO-acid* (IX), $\text{C}_{20}\text{H}_{32}\text{O}_3$, m.p. $166\text{--}167^\circ$ [*semicarbazone*, m.p. about 296° (decomp.)], transformed by NaOBr into CBr_4 and (VIII), which is also obtained by more drastic oxidation of (IV). The arrangements $\text{C}_{17}\text{H}_{28}\begin{Bmatrix} -\text{C:CH}_2 \\ -\text{CH}_2 \end{Bmatrix}$ in (I) and

$\text{C}_{17}\text{H}_{23}\begin{Bmatrix} -\text{CMe} \\ -\text{CH} \end{Bmatrix}$ in (IV) are thus indicated. Ozonis-



ation of (I) in CCl_4 yields the *diozonide*, $\text{C}_{20}\text{H}_{32}\text{O}_6$, converted by boiling H_2O into CH_2O and HCO_2H and (VII) with its (?) *peroxide*, m.p. $186\text{--}187^\circ$ (decomp.), which does not react with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ or NH_2OH . Similarly (IV) affords a *diozonide* which is decomposed to traces of HCO_2H , (IX), and its *peroxide*, m.p. $186\text{--}190^\circ$ (decomp.). The constitution A is therefore assigned to (I) and either B or C to (IV). H. W.

Phenolic acid, $\text{C}_{16}\text{H}_{14}\text{O}_8$, from *Oospora sulphurea-ochracea*.—See A., III, 99.

Catalytic preparation of α -pyroabietic acid. E. E. FLECK and S. PALKIN (Science, 1937, 85, 126).— $\text{Pd}\cdot\text{charcoal}$ catalyses the production of this acid from α -pimaric acid, *l*-abietic acid (Schulz), mixed rosin acids and rosins from *Pinus palustris*, *P. caribaea*, and *P. pinaster*. The catalysis is most effective at 250° , but occurs even at 200° . $\text{Pt}\cdot\text{charcoal}$, $\text{Ni}\cdot\text{charcoal}$, and, to a smaller extent, activated charcoal also catalyse the formation of pyroabietic acid. L. S. T.

Biochemistry of micro-organisms. LIII. Crystalline colouring matters of *Fusarium culmorum* (W. G. Smith), Sacc., and related forms. J. N. ASHLEY, B. C. HOBBS, and H. RAISTRICK (Biochem. J., 1937, 31, 385—397).—The following pigments were isolated: *rubrofusarin*, $C_{15}H_{12}O_5$, m.p. 210—211°, containing $\cdot OMe$ {*mono*-, m.p. 211°, and *diacetate*, m.p. 260°; *Br₂-derivative*, m.p. 244°; *Me*, m.p. 203—204°, and *Me₂ ether*, m.p. 187—188° [ferrichloride, m.p. 183—184° (decomp.)]}; *nor-rubrofusarin*, m.p. >280° (*diacetate*, m.p. 204°), *aurofusarin*, $C_{30}H_{20}O_{11} \cdot H_2O$ (?), m.p. >360°, containing 2 *OMe* (*benzoate*, m.p. 212—215°; *p-bromobenzoate*, decomp. 304°; *dianisate*), reduced (H_2 -Pd-C or $NHPh \cdot NH_2$) to the H_4 -derivative, m.p. >360° [*benzoate*, m.p. 368—369° (decomp.); *p-bromobenzoate*, m.p. 357° (decomp.); *hexa-anisate*, m.p. 338° (decomp.)], and *culmorin*, $C_{15}H_{26}O_2$, m.p. 174—175°, [α_{D}^{20}]₄₀₁ -14.45° in $CHCl_3$ (*diacetate*, m.p. 90—91°; *di-p-bromobenzoate*, m.p. 102—103°). F. O. H.

Wax and resin of *Taraxacum* root. S. INOUE (J. Soc. Chem. Ind. Japan, 1937, 40, 23—24B).—The dry root of *T. platycarpum* yields to Et_2O a *resin*, m.p. 40°, [α_D^{20}] +19.16°, and a *wax*, m.p. 152°, [α_D^{20}] +47.2°; from the unsaponifiable matter of the wax is isolated a *substance*, $C_{22}H_{36}O$, [α_D^{20}] +66.39° (*acetate*, m.p. 179°; *benzoate*, m.p. 260°), showing sterol reactions. J. D. R.

Lactucarium. III. Bitter substances of the sap of *Lactuca virosa*. K. H. BAUER and K. BRUNNER (Ber., 1937, 70, [B], 261—263; cf. A., 1929, 1181).—Treatment of the fresh sap with $EtOH$ and extraction with boiling H_2O of the residue left after removal of $EtOH$ gives *neolactucin* (I), $C_{23}H_{25}O_7 \cdot H_2O$, m.p. 147—148°, which immediately reacts with Br and $C(NO_2)_4$, readily reduces Fehling's solution and $Ag_2O \cdot NH_3$, but does not give an oxime or semicarbazone. It does not contain OMe but 3 OH (Zerevitinov) are present. Ill-defined products are obtained with CH_2N_2 and non-cryst. substances by hydrolysis with KOH . It yields a *dibenzoate*, m.p. 174—176°. The fresh sap contains (I) but not *lactucin* (II), $C_{18}H_{20}O_6$, whereas both are present in technical lactucarium. (II) is unsaturated, reduces Fehling's solution very readily, and does not react with aldehydic or ketonic reagents. It contains 3 OH (Zerevitinov); OMe is absent. It does not react with CH_2N_2 . It requires 3 mols. of KOH for hydrolysis, whereby it yields non-cryst. substances. H. W.

Lichen substances. LXXIV. Usnic acid. II. Y. ASAHINA and M. YANAGITA (Ber., 1937, 70, [B], 67—70; cf. A., 1936, 1262).—*Me* pyrousnate Me_2 ether is converted by amyl nitrite and $NaOEt$ into the *oximino-derivative*, m.p. 191°, hydrolysed to the corresponding *acid*, m.p. about 116° (decomp.), which loses CO_2 and H_2O when boiled with Ac_2O , giving 1-cyano-3:5-dimethoxy-2:4-dimethylbenzofuran, m.p. 126°. The latter is hydrolysed to 3:5-dimethoxy-2:4-dimethylbenzofuran-1-carboxylic acid, m.p. 220° (decomp.), decarboxylated by Cu powder in quinoline at 220° to 3:5-dimethoxy-2:4-dimethylbenzofuran [*picrate*, (I), m.p. 94°]. *Me* 3:5-dimethoxy-*p*-toluate and $N_2H_4 \cdot H_2O$ in $EtOH$ at 100° give the corresponding *hydrazide*, m.p. 189°, whence the

azide, m.p. about 105° (decomp.), and 3:5-dimethoxy-*p*-tolylurethane (II), m.p. 98°. Treatment of (II) with KOH - $EtOH$ followed by HCl leads to 3:5-dimethoxy-*p*-toluidine, m.p. 130° (*hydrochloride*), whence 3:5-dimethoxy-*p*-cresol, m.p. 150°, which with CH_2ClAc and anhyd. K_2CO_3 in boiling $COMe_2$ yields 3:5-dimethoxy-*p*-tolylloxyacetone, m.p. 67°. This with conc. H_2SO_4 at 0° affords a coumarone giving a picrate identical with (I). The relative positions of *Me* and $\cdot CH_2 \cdot CO_2H$ in the furan nucleus of pyrousnic acid are thereby confirmed (*loc. cit.*). H. W.

Resin acid series. I. Synthesis of Vocke's unsaturated acid, $C_{10}H_{14}O_4$. H. N. RYDON (J.C.S., 1937, 257—259).—*Et* 2-hydroxy-2-cyano-1:3-dimethylcyclohexane-1-carboxylate, m.p. 75°, prepared from the keto-ester, is dehydrated ($SOCl_2$) to the unsaturated cyano-ester, hydrolysed by HCl to 2-carboxy-1:3-dimethyl-1:3-cyclohexanolide, m.p. 145° (cf. Vocke, A., 1932, 1036, lactic acid), and by KOH to 2-cyano-1:3-dimethyl-1:3-cyclohexanolide, m.p. 168—169°, and 1:3-dimethyl- Δ^2 -cyclohexene-1:2-dicarboxylic acid, identical with the $C_{10}H_{14}O_4$ acid obtained by Vocke. The $C_{11}H_{16}O_6$ acid formed by oxidation of abietic acid must be 1:3-dimethylcyclohexane-1:2:3-tricarboxylic acid. F. R. S.

Resinols. IV. Structure of α -amyrenol. F. S. SPRING and T. VICKERSTAFF (J.C.S., 1937, 249—252).— α -Amyrenyl benzoate is oxidised (CrO_3) to α -amyrenonyl benzoate, m.p. 266°, hydrolysed to α -amyrenol (I), dehydrated (PCl_5) to α -amyradienone I, m.p. 197°, [α_D^{20}] +166° in $CHCl_3$, and II, m.p. 156°, [α_D^{20}] +153° in $CHCl_3$. Reduction ($Na-C_5H_{11} \cdot OH$) of (I) gives dehydro- α -amyrenol, m.p. 160°, the *acetate*, m.p. 170°, of which is converted (BzO_2H) into dehydro- α -amyrenyl acetate oxide, m.p. 192°. (I) is dehydrogenated (Se) to 1:2:7- $C_{10}H_5Me_3$, 1:2:5:6- $C_{10}H_4Me_4$, 1:5:6:2- $C_{10}H_4Me_3 \cdot OH$, and $C_{25}H_{30}$ (? trimethylpicene), m.p. 306°. The mol. structure of α -amyrenol is discussed in the light of these observations. F. R. S.

Resinol of *Olea Cunninghamii* (Maire). L. H. BRIGGS and A. F. FRIEBERG (J.C.S., 1937, 271—273).—The cryst. resin from *O. Cunninghamii* has been identified as *isoolivil* (I), which has been methylated (excess of Me_2SO_4) to the *Me₃ ether*, m.p. 153—154°, [α_D^{20}] +26.23° in $CHCl_3$. Demethylation (HI) of (I) affords a small yield of pyrocatechol. The structure of (I) is discussed. F. R. S.

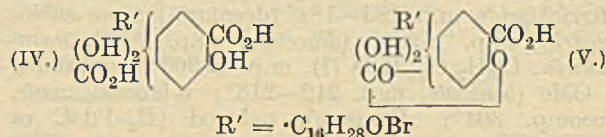
Resin components of galbanum. I. W. KUNZ and E. WÜLDICKE (Ber., 1937, 70, [B], 359—367).—The material is shaken with Et_2O whereby essentially gum remains undissolved. The solution is extracted successively with 5% Na_2CO_3 and 2% $NaOH$. The residual solution when evaporated to dryness and then treated with light petroleum gives the neutral resin (I). Fractional pptn. by light petroleum from $CHCl_3$ of the portion sol. in Na_2CO_3 gives *cryst. galbaresinic acid* (II), $C_{24}H_{30}O_5$ (possibly $C_{24}H_{28}O_5$ or $C_{23}H_{28}O_5$), m.p. 93—95°, which dissolves in $NaHCO_3$ and, according to titration and by Zerevitinov's method, contains 1 CO_2H . With CH_2N_2 it gives a *Me* ester, hydrolysed to (II). When heated at 280—300°/vac. or hydrolysed with $AcOH-H_2SO_4$ (II)

yields umbelliferone (III). A lactone group is present in (II). Hydrogenation (Pt in AcOH) in 0.1M solution with 50% of catalyst causes rapid absorption of 1 H₂, then slower and regular action followed by slow absorption of the fourth mol. indicating the saturation of the coumarin double linking. In 0.025M solution with 75% catalyst 7 H₂ are absorbed. Fractional pptn. of (I) by light petroleum from Et₂O gives materials which become partly cryst. after long preservation and from which *neutral substance* I (IV), m.p. 175–176°, and *neutral substance* II (V), m.p. 155–156°, are isolated. Both are C₂₄H₃₀O₄ or, possibly, C₂₃H₂₈O₄. (IV) and (V) are lactones which gives (III) when hydrolysed by AcOH–H₂SO₄. (IV) is transformed by molten KOH into β-resorcylic acid. Hydrogenation [Pt (70%) in AcOH] of (IV) or (V) is accompanied by rapid union with 2 H₂ followed by slow absorption which ceases after union with 7 H₂. In conc. solution (IV) absorbs 1 H₂ rapidly and reaction ceases after union with 4 H₂. The presence of ethers of (III) with a chain of 3 isoprene links is thus indicated in (IV) and (V). (IV) contains 1 active H (Zerevitinov). (IV) and (V) react with Ac₂O giving clear masses from which the initial materials are regenerated by hydrolysis. Galbanic acid, C₁₅H₂₀O₂, m.p. 155–156°, is isolated from technical galbanum in very small amount; titration with Br shows the presence of 1 double linking. H. W.

New bitter principle from a South West African *Cucumis* species. C. RIMINGTON and D. G. STEYN (South African J. Sci., 1935, 32, 137–141; Chem. Zentr., 1936, i, 2757).—From the fruit is isolated a *substance* (I), C₂₈H₄₂O₈, of very bitter taste, m.p. 137° with loss of H₂O yielding a *substance*, C₂₈H₄₀O₇, m.p. 167–170°, [α]_D²⁰ +73.77° in EtOH. (I) reacts with 2 mols. of PhNCO, contains 1 CO (2:4-dinitrophenylhydrazones, m.p. 191–193°), and no OMe; the action of KOH indicates the possible presence of 2 lactone rings. H. N. R.

Elaterin. W. BORSCHKE and K. DIACONT (Annalen, 1936, 528, 39–57).—Elaterin, C₂₈H₃₈O₇, m.p. 227–228°, [α]_D¹⁹ –36.6° in CHCl₃, contains 1 Ac and 2 OH and is probably (I). With hot 0.5N-NaOH in

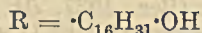
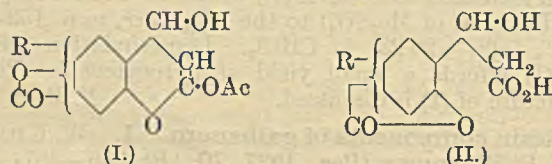
[α]_D¹⁷ +77.52° in C₅H₅N. A little HCl in hot AcOH converts (IV) into (V) and an *isomeride*, m.p. 205–240° (decomp.), of (IV). (IV) gives the following derivatives of (V): with CH₂N₂ in COMe₂ or HCl–MeOH the *Me* ester (VI), m.p. 240° (decomp.); with Ac₂O at 100° the *Ac*, m.p. 180°, and with Ac₂O–H₂SO₄ the *Ac*₂ derivative, m.p. 240°, which give the same *Me* ester, C₂₈H₃₁O₈Br·OMe, m.p. 242–243° (decomp.). H₂–Pd–C and (V) in MeOH give the *lactonic acid*



(VII), C₂₄H₃₀O₇, m.p. 260° [*Me* ester, m.p. 240°; *Ac*₂ derivative, m.p. 210° (decomp.)], also obtained by hydrogenation and hydrolysis of (VI); HI–AcOH–P and (VI) give, however, (?) an *isomeride*, m.p. 264°, of (VII). When heated above the m.p., (VII) gives CO₂ and H₂O (1 mol. each) and a *substance*, C₂₃H₃₀O₄, m.p. 230°, sol. in dil. NaOH. CrO₃ (4 O) and (VII) give a poor yield of an *acid*, C₂₄H₂₈O₈, m.p. 284°, and the *Me* ester of (VII) gives a *substance*, C₂₄H₃₂O₈, m.p. 278°, which reacts with 2:4-(NO₂)₂C₆H₄·NH·NH₂. Br and (III) give a mixture, which with fuming HNO₃ in hot AcOH gives two *substances*, C₂₄H₂₅O₆NBr₄, m.p. 290° and 276° (decomp.). (II) and (III) with NaOAc or AgOAc in hot AcOH give *substances*, C₂₄H₂₈O₄Br₆, m.p. varies (200–205°), [α]_D varies, –13.68° to –32.86° in C₅H₅N, with a dextrorotatory resin and, in some cases, *substances*, m.p. 222° and (dextrorotatory) 260°. R. S. C.

Isolation of an icterogenic substance from *Lippia rehmanni*, Pears. C. RIMINGTON and J. I. QUIN (South African J. Sci., 1935, 32, 145–151; Chem. Zentr., 1936, i, 2757–2758).—From the dried plant is isolated *icterogenin*, C₃₁H₄₆O₅, m.p. 236–239°, [α]_D²⁰ +72.0° in EtOH, containing 1 CO₂H, 1 CO (2:4-dinitrophenylhydrazones, m.p. 212–214°), and no OMe or OH; its physiological action is described. H. N. R.

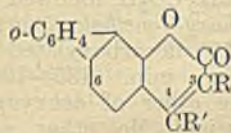
Synthesis of coumarins and chromones from halogeno- and nitro-cresols. D. CHAKRAVARTI and B. C. BANERJEE (J. Indian Chem. Soc., 1936, 13, 619–626).—The presence of Cl and NO₂ in cresols decreases their reactivity in the Pechmann coumarin synthesis, but increases that in the Simonis chromone synthesis. α-Substituents in the CH₂Ac·CO₂Et hinder the former, but have no effect on the latter, reaction. Yields in the Simonis reaction are >10–15%. The following are prepared, figures in parentheses being the m.p. of the 2-styrylchromones, prepared by PhCHO and NaOEt–EtOH: 6-chloro-2:8-dimethyl-, m.p. 130° (176–178°), -2:3:8-trimethyl-, m.p. 113° (164°), -2:8-dimethyl-3-ethyl-, m.p. 128° (154°), -2:8-dimethyl-3-propyl-, m.p. 120° (135°), -2:3:7-trimethyl-, m.p. 94° (153°), -2:7-dimethyl-3-ethyl-, m.p. 113° (155°), and -2:7-dimethyl-3-propyl-, m.p. 92° (cryst.), 8-chloro-2:3:6-trimethyl-, m.p. 150° (183°), and -2:6-dimethyl-3-ethyl-, m.p. 105° (132°), 6-nitro-2:3:8-trimethyl-, m.p. 245° (225°), -2:8-dimethyl-3-ethyl-, m.p. 233° (205°), and -2:8-dimethyl-3-propyl-, m.p. 200°, 8-nitro-2:7-dimethyl-, m.p. 130°,



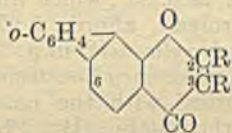
N₂ it gives crude, amorphous elateric acid (II), m.p. 73–75°, from which NaOH removes *ecballium acid* (III), C₂₆H₃₈O₇, m.p. 257° (decomp.), [α]_D¹⁸ –57.9° in COMe₂ [*Me* ester, m.p. 210°; *Ac*, m.p. 265° (decomp.), *Ac*₂, m.p. 246° (decomp.), and *Ac*₃ derivative, m.p. 257–258°], leaving an “exhausted” (II). (III) and crude (II) give the same degradation products, but “exhausted” (II) gives none of them (except, in poor yield, with Br). NaOBr and (III) give CBr₄, a *bromodicarboxylic acid* (IV), C₂₄H₃₃O₈Br, m.p. about 240° (decomp.), [α]_D¹⁷ +33.5° in COMe₂, and a *bromolactonic acid* (V), C₂₄H₃₁O₇Br, m.p. 250° (decomp.),

and -2:7-dimethyl-3-ethyl-, m.p. 137°, -chromone; 8-chloro-4:6-dimethyl-, m.p. 105°, -3:4:6-trimethyl-, m.p. 152°, and -4:6-dimethyl-3-ethyl-, m.p. 146°, 3:8-dichloro-4:6-dimethyl-, m.p. 110°, 6-chloro-4:7-dimethyl-, m.p. 208°, -3:4:7-trimethyl-, m.p. 146°, -2:3:7-trimethyl-, m.p. 94°, and -4:7-dimethyl-3-ethyl-, m.p. 136°, and 3:6-dichloro-4:7-dimethyl-, m.p. 210°, -coumarin; Et 6-chloro-7-methylcoumarin-4-, m.p. 185—188°, and 6-chloro-4:7-dimethylcoumarin-3-acetate, m.p. 110—112°. R. S. C.

Synthesis of coumarins and chromones from 4-chloro- and 4-bromo-1-naphthol. D. CHAKRAVARTI and P. N. BAGCHI (J. Indian Chem. Soc., 1936, 13, 649—656).—4:1-C₁₀H₆Cl·OH (modified prep.) and, less smoothly, 4:1-C₁₀H₆Br·OH with CH₂Ac·CO₂Et or CHClAc·CO₂Et give the naphthapyrone (I) with all condensing agents; CHRAc·CO₂Et (R = alkyl), however, gives (I) with H₂SO₄, but the chromone (II) with P₂O₅. Malic acid in H₂SO₄ gives



(I.)



(II.)

readily 6-chloro-1:2-α-naphthapyrone, m.p. 163°, converted by HgO-KOH into 7-chloro-α-naphtho-coumaric (β-1-chloro-4-hydroxynaphthyl-3-acrylic) acid, m.p. 185° (decomp.). The following are described, figures in parentheses being the m.p. of the 2-styryl-chromones: 6-chloro-4-methyl-, m.p. 219°, -3:4-dimethyl-, m.p. 203—204°, -4-methyl-3-ethyl-, m.p. 129—130°, -4-methyl-3-propyl-, m.p. 104—105°, -4-methyl-3-isobutyl-, m.p. 136—138°, -3-benzyl-4-methyl-, m.p. 200°, -4-phenyl-, m.p. 164°, and -3-phenyl-4-methyl-, m.p. 215—216°, -1:2-α-naphthapyrone; 6-chloro-4-methyl-1:2-α-naphthapyrone-3-, m.p. 181—184°, and 6-chloro-1:2-α-naphthapyrone-4-acetic acid, m.p. 212° (decomp.); 3:6-dichloro-4-methyl-1:2-α-naphthapyrone, m.p. 257°; 6-bromo-4-methyl-, m.p. 208°, -3:4-dimethyl-, m.p. 187—189°, and -3-benzyl-4-methyl-, m.p. 175—176°, -1:2-α-naphthapyrone; 6-chloro-2:3-dimethyl-, m.p. 181—183° (188—190°), -2-methyl-3-ethyl-, m.p. 167—168° (194—195°), -2-methyl-3-propyl-, m.p. 126—127° (228°), and -2-methyl-3-isobutyl-, m.p. 120—122° (235—236°), -1:4-α-naphthapyrone; 6-bromo-2:3-dimethyl-1:4-α-naphthapyrone, m.p. 211—212° (233°). R. S. C.

Ayapin. P. K. BOSE and S. K. GHOSH (Current Sci., 1936, 5, 295; cf. this vol., 70).—Ayapin, m.p. 219—220°, from the leaves of *Eupatorium ayapana*, Vent., is 6:7-methylenedioxycoumarin. With Na-Hg it gives a H₂-compound, m.p. 175—177°; with Br followed by EtOH-KOH, it affords an acid, m.p. 269—271°, probably a coumarilic acid. J. L. D.

Limited applicability of Kostanecki's reaction. D. CHAKRAVARTI and P. N. BAGCHI (J. Indian Chem. Soc., 1936, 13, 689—696).—With NaOAc-Ac₂O, both aceto- and propiono-naphthols yield chromones, not coumarins. Thus 4-chloro-2-aceto-α-naphthol (I), m.p. 121° (phenylhydrazones, m.p. 158—159°; semicarbazone, m.p. 275°; Me ether, m.p. 66—67°; Bz derivative, m.p. 123—124°) (from 4-chloro-α-naphthyl Me

ketone and AlCl₃), gives 6-chloro-3-aceto-2-methyl-1:4-β-α-naphthapyrone, m.p. 188—189° (cf. A., 1932, 858). Similarly 4-chloro-2-propion-α-naphthol (II), m.p. 90—91° (semicarbazone, m.p. <275°) (from 4-chloro-α-naphthol, EtCOCl, and AlCl₃) gives 6-chloro-2:3-dimethyl-1:4-β-α-naphthapyrone (see above). With Bz₂O-NaOBz, (I) also gives a chromone, 6-chloro-3-benzoyl-2-phenyl-1:4-β-α-naphthapyrone, m.p. 224°, with a substance, m.p. 152—154°. With EtCO₂Na-(EtCO)₂O, and CH₂Ph·CO₂Na-(CH₂Ph·CO)₂O, however, (I) forms the coumarins, 6-chloro-3:4-dimethyl- and -3-phenyl-4-methyl-1:2-β-α-naphthapyrone (see above). With the former reagent, (II) yields 6-chloro-3-methyl-4-ethyl-1:2-β-α-naphthapyrone, m.p. 158—160°. (I) condenses with HCO₂Et (Na) to 4-chloro-2-hydroxymethyleneaceto-α-naphthol, m.p. 146—147° (Cu salt) [converted by NHPh·NH₂ into 1-phenyl-3-(4'-chloro-1'-hydroxy)-β-naphthylpyrazole, m.p. 184°], which with H₂SO₄ yields 6-chloro-1:4-β-α-naphthapyrone, m.p. 170—171°. Similarly 4-bromo-2-aceto-α-naphthol, m.p. 126—127° (cf. A., 1910, i, 48) (benzylidene derivative, m.p. 176—177°), from 4-bromo-α-naphthyl Me ketone and AlCl₃, gives 4-bromo-2-hydroxymethyleneaceto-α-naphthol, m.p. 147—148° (Cu salt), from which 1-phenyl-3-(4'-bromo-1'-hydroxy)-β-naphthylpyrazole, m.p. 180—181°, is obtained. With the appropriate benzaldehydes and NaOEt, (I) yields the chalkones, 4-chloro-2-cinnamoyl-α-naphthol, m.p. 186—187°, and its 4'-methoxy-, m.p. 196—198°, and 3':4'-dimethoxy-, m.p. 174—176°, -derivatives. E. W. W.

Structure of xanthone and the orientation of its α- and β-dinitro-derivatives. (MRS.) C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1937, 196—202).—The dipole moment of xanthone is found to be 3.11. The excess of this val. over that calc. from Ph₂O and CPh₂ is almost completely due to electrostatic induction effects operating between different groups in the mol. The amount of such induction is calc. The observed moments of two 2:7-disubstituted xanthenes show that the links holding the substituents in each case are at 141—142° to each other, showing that a fixation of double and single linkings occurs in the xanthone skeleton. On this basis the moments of the four possible dinitroxanthenes have been calc.; α-dinitroxanthone is a slightly impure specimen of 2:4-dinitroxanthone. F. R. S.

Reaction between triarylmethyl halides and magnesium phenyl bromide. III. 9-Phenyl-xanthyl chloride. C. S. SCHOEPFLE and J. H. TRUESDALE (J. Amer. Chem. Soc., 1937, 59, 372—377; cf. A., 1932, 1240; 1936, 834).—9-Phenyl-xanthyl chloride (I) and MgPhBr (2 mols.) give 9-phenyl- (II) (13—21%), 3:9-diphenyl- (III) (34—51%), 9:9-diphenyl- (IV) (traces), and 3:6:9-triphenyl- (V) (3—14%), -xanthenes. (III) and (IV) are the expected products and arise owing to reaction of (I) in the quinonoid and benzenoid (limited extent) form, respectively. (II) and (V) are probably formed thus: some (III) reacts with unchanged (I) to give (II) and 3:9-diphenylxanthyl chloride [which then reacts with MgPhBr to form (V)]. The 9-Ph group does not react in the quinonoid form, since (VII) (below) could not be detected. The mixture of (III)

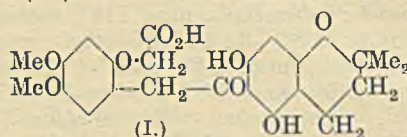
and (V) is difficultly separable and its composition is determined by thermal analysis.

Xanthone and $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{MgBr}$ give 9- p -diphenylxanthanol (VI), m.p. 178—179°, converted by boiling $\text{HCO}_2\text{H} + \text{HCO}_2\text{Na}$ into 9- p -diphenylxanthene (VII), m.p. 206—207°. 3-Chloro-4-nitrodiphenyl, m.p. 78.5—79.5° (from 4:3- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{N}_2\text{Cl}$ and C_6H_6 in 40% NaOH), is reduced (SnCl_2 , conc. HCl , EtOH) to the NH_2 -derivative [more conveniently prepared by Scarborough and Waters' method (A., 1926, 512)], which is converted (Sandmeyer) into 3-chloro-4-cyanodiphenyl, m.p. 101—101.5°. This is hydrolysed (aq. $\text{EtOH}\text{--NaOH}$) to 3-chlorodiphenyl-4-carboxylic acid, m.p. 166.5—167°, the K salt (VIII) of which with $\text{PhOH}\text{--NaOPh}$ and Cu-bronze at 150° (bath) gives 3-phenoxydiphenyl-4-carboxylic acid, m.p. 169.5—170°, converted by successive treatment with PCl_5 and AlCl_3 in C_6H_6 into 3-phenylxanthone, m.p. 141—141.5°. This and MgPhBr in $\text{Et}_2\text{O}\text{--C}_6\text{H}_6$ afford 3:9-diphenylxanthanol, m.p. 128.5—129°, converted [as for (VI)] into 3:9-diphenylxanthene, m.p. 146.5—147°. (VIII) and $m\text{-C}_6\text{H}_4\text{Ph}\cdot\text{ONa}$ at 150—180° similarly give 3- m -diphenylxanthene-4-carboxylic acid, m.p. 186—187°, converted through its chloride into 3:6-diphenylxanthone (IX), m.p. 193.5—194.5°, and some of the 1:6-isomeride (not obtained pure). 3:6:9-Triphenylxanthanol, decomp. 238—239° [from (IX) and MgPhBr], is converted [as for (VI)] into 3:6:9-triphenylxanthene, decomp. 220°. 3-Bromo-4-methyldiphenyl, b.p. 123—123.5°/2 mm., m.p. 9° (from 4:3- $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{N}_2\text{Cl}$ and C_6H_6 in 40% NaOH at <9°), could not be oxidised satisfactorily to 3-bromodiphenyl-4-carboxylic acid. H. B.

Synthesis of rotenone and its derivatives. XI. Tetrahydrotubanol. A. ROBERTSON and T. S. SUBRAMANIAM. XII. 2:2-Dimethyl- Δ^3 -chromen residue of toxicarol. W. BRIDGE, R. G. HEYES, and A. ROBERTSON (J.C.S., 1937, 278—279, 279—285).—XI. The isovaleric ester of 7-hydroxy-4-methylcoumarin gives (AlCl_3) 7-hydroxy-8-isovaleryl-4-methylcoumarin, m.p. 109—110° [o-chlorobenzoylhydrazone, m.p. 128—130° (decomp.)], hydrolysed to 2:6-dihydroxyisovalerophenone, m.p. 67—68°. Reduction ($\text{Zn}\text{--Hg}$) of the ketone affords tetrahydrotubanol.

XII. Oxidation (KMnO_4) of dehydrotoxicarol acetate gives 2-hydroxy-4:5-dimethoxybenzoic acid, rissic acid, and a neutral substance, m.p. 149°. Hydrolytic fission (KOH) of dihydrotoxicarolic acid (I) affords 5:7-dihydroxy-2:2-dimethylchroman (II), m.p. 162—163° (diacetate, m.p. 86°). $\beta\beta$ -Dimethylacryl chloride, phloroglucinol, and AlCl_3 yield 5:7-dihydroxy-2:2-dimethylchromanone, m.p. 198° (2:4-dinitrophenylhydrazone, m.p. 277—278°), and in certain conditions a substance, $\text{C}_{16}\text{H}_{18}\text{O}_5$, m.p. 134° (2:4-dinitrophenylhydrazone, m.p. 267—268°). The chromanone is methylated ($\text{MeI}\text{--K}_2\text{CO}_3$) to 5:7-dimethoxy-2:2-dimethylchromanone (III), m.p. 104.5—105° [2:4-dinitrophenylhydrazone, m.p. 240°; semicarbazone (?), m.p. 245°], and is reduced to the chroman, identical with the natural product (II). α -Bromoisovaleryl chloride, phloroglucinol, and AlCl_3 give 4:6-dihydroxy-2-isopropyl-3-coumaranone, m.p. 196°, methylated to 4:6-dimethoxy-2-isopropyl-(β -) coumaranone (IV), b.p. 140—150°/0.1 mm. (2:4-

dinitrophenylhydrazone, m.p. 185°), also obtained from $\text{Et } \alpha\text{-bromoisovalerate}$ and phloroglucinol Me_2 ether. (III) and (IV) are isomeric and not identical. This

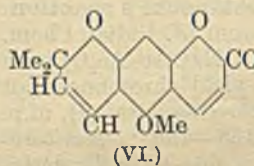


result affords conclusive proof that toxicarol contains the 2:2-dimethyl- Δ^3 -chromen system and makes it possible to assign the structure for (I). A mechanism for the production of COMe_2 by scission of 2:2-dimethyl- Δ^3 -chromens is suggested. F. R. S.

Constituents of *Zanthoxylum americanum* (Mill). III. Constitution of xanthoxyletin. A.

ROBERTSON and T. S. SUBRAMANIAM (J.C.S., 1937, 286—292).—C-Methylphloroglucinol $\beta\text{-Me}_2$ ether and HCN give 2-hydroxy-4:6-dimethoxy-5-methylbenzaldehyde, m.p. 85°, which with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, followed by hydrolysis, affords 5:7-dimethoxy-6-methylcoumarin-3-carboxylic acid, m.p. 233—234°, decarboxylated to 5:7-dimethoxy-6-methylcoumarin, m.p. 135—136°, identical with the natural Me ether of deoxyapoxanthoxyletin (I). Phloroglucinol Me ether and HCN yield 2:4-dihydroxy-6-ethoxybenzaldehyde, m.p. 169.5° (2:4-dinitrophenylhydrazone, m.p. 263—264°), reduced ($\text{Pd}\text{--H}_2$) to C-methylphloroglucinol $\beta\text{-Et}$ ether, m.p. 130°, which is converted (Gattermann) into 2:6-dihydroxy-4-ethoxy-3-methylbenzaldehyde, m.p. 196—197° (2:4-dinitrophenylhydrazone, m.p. 260—261°), methylated to the 2-hydroxy-6-methoxy-compound (cf. Curd *et al.*, A., 1933, 609, 831). The methoxy-aldehyde and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ afford 5-methoxy-7-ethoxy-8-methylcoumarin-3-carboxylic acid, m.p. 238—239°, decarboxylated to the coumarin, m.p. 167°, which on fusion and methylation gives the Me ester, m.p. 78°, hydrolysed to 2:6-dimethoxy-4-ethoxy-3-methylcinnamic acid (II), m.p. 164—165°. Ethylation of (I) yields an Et ether, m.p. 135°, converted by hydrolysis and methylation into Me 2:6-dimethoxy-4-ethoxy-3-methylcinnamate, m.p. 78.5°, hydrolysed to (II). From this it follows that (I) must be 7-hydroxy-5-methoxy-6-methylcoumarin.

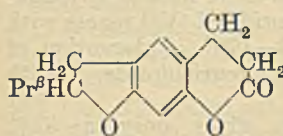
5:7-Dihydroxy-2:2-dimethylchroman and $\text{HCN}\text{--HCl}$ give a substance, m.p. 123—124°, and 5:7-dihydroxy-8-formyl-2:2-dimethylchroman (III), m.p. 179—180°. Reduction ($\text{Zn}\text{--AcOH}$) of 5:7-dimethoxy-2:2-dimethylchromanone affords the chroman, b.p. 105°/0.05 mm., which with HCN gives 5:7-dimethoxy-8-formyl-2:2-dimethylchroman (semicarbazone, m.p. 217—218°; 2:4-dinitrophenylhydrazone, m.p. 242—243°), identical with that obtained by methylation of (III). Ozonolysis of dihydroxanthoxyletin gives 7-hydroxy-5-methoxy-6-formyl-2:2-dimethylchroman (IV), m.p. 85—86°, methylated to the 5:7-dimethoxy-compound (V), m.p. 81—82° (semicarbazone, m.p. 215.5—216.5°; 2:4-dinitrophenylhydrazone, m.p. 215—216°), also obtained by oxidation (KMnO_4) of O-methyldihydroxanthoxyletinic acid. (V) is oxidised (KMnO_4) to 5:7-dimethoxy-2:2-dimethylchroman-6-carboxylic acid, m.p. 142—143° (de-



comp.). This establishes the presence of a chromen residue in xanthoxyletin. *Tetrahydroxanthoxyletin*, m.p. 121°, is obtained by reduction of the H_2 -compound. (IV) and $CN \cdot CH_2 \cdot CO_2H$ afford *dihydroxanthoxyletin-3-carboxylic acid*, m.p. 139—140°, decarboxylated to the coumarin. Xanthoxyletin must be represented by (VI). F. R. S.

Furano-compounds. I. Synthesis of bergapten. W. N. HOWELL and A. ROBERTSON (J.C.S., 1937, 293—294).—2 : 4-Dihydroxy-6-methoxybenzaldehyde and $CN \cdot CH_2 \cdot CO_2H$ give an acid, hydrolysed to *7-hydroxy-5-methoxycoumarin-3-carboxylic acid*, m.p. 264°, converted (Cu) into *7-hydroxy-5-methoxycoumarin* (I), m.p. 246°. *apoXanthoxyletin* (II) and $CH_2Br \cdot CO_2Et$ form the *Et* ester, m.p. 130°, hydrolysed to *7-hydroxy-5-methoxy-6-formylcoumarin-7-O-acetic acid*, m.p. 242° (decomp.), which on cyclisation and decarboxylation (Ac_2O - $NaOAc$) affords bergapten, identical with the natural product. The conversion of (I) into (II) has not yet been achieved. F. R. S.

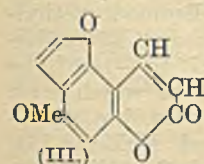
Catalytic dehydrogenation processes. X. Dehydrogenation of dihydrocoumarins. E. SPÄTH and F. GALINOVSKY (Ber., 1937, 70, [B], 235—238).—Dehydrogenation of dihydrocoumarins is effected by heating with Pd-sponge at 200—250° for 4—8 hr. or for a longer period at 200—210° if the materials are sensitive to high temp. Separation of the products is frequently effected by distillation or sublimation or, if these methods fail, by dissolution in alkali followed by acidification at room temp. The coumaric acids rapidly passed into the original coumarins whereas the OH-acids from the dihydrocoumarins are more stable and can be removed from Et_2O by aq. Na_2CO_3 . Dihydrocoumarin and dihydroumbelliferone (I) give coumarin and umbelliferone in 40% and 60—65% yield, respectively. Better results are obtained with



3 : 4-dihydrodaphnetin and 3-phenyl-3 : 4-dihydrocoumarin (II), m.p. 122°. (I) and (II) yield $p\text{-}C_6H_4Et \cdot OH$ and $(CH_2Ph)_2$ in small amount. Tetrahydro-osthol

affords dihydro-osthol in 35% yield. Dehydrogenation of di- and tetra-hydroisopropylpsoralene leads to anhydronodaphnetin, which therefore has the annexed constitution. H. W.

Natural coumarins. XXII. Synthesis of allobergapten. E. SPÄTH, F. WESSELY, and G. KUBICZEK (Ber., 1937, 70, [B], 243—248).—Treatment of 4 : 6-dihydroxycoumaranone (I) with Ac_2O at 100° gives 4 : 6-diacetoxycoumaranone, m.p. 125°, converted by Ac_2O containing $AcCl$ at 100° into 3 : 4 : 6-triacetoxycoumaranone (II), m.p. 104°. (I) is transformed by boiling Ac_2O into a substance, m.p. 172—173°, hydrolysed by 3% H_2SO_4 at 100° to (I). (II) is hydrogenated (Pd-sponge in $AcOH$) to



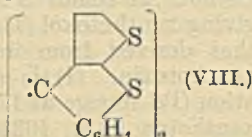
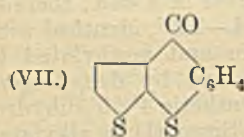
3 : 4 : 6-triacetoxycoumaran, m.p. 81°, which is condensed with *Et* sodioformylacetate, thus adding the lactone group of the coumarin ring and eliminating *Ac*; the product is distilled in a vac. and then treated with CH_3N_2 , thus giving

H_2O_2 to furan-2 : 3-dicarboxylic acid and gives the reactions typical of a coumarin. The presence of 2 double linkings is established by its hydrogenation to *tetrahydroallobergapten*, m.p. 183°. For comparison, *tetrahydrobergapten*, m.p. 115°, and *tetrahydroisobergapten*, m.p. 166°, are prepared. The mother-liquors from (III) appear to contain bergapten or dihydrobergapten. H. W.

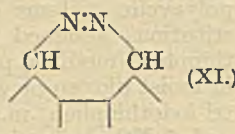
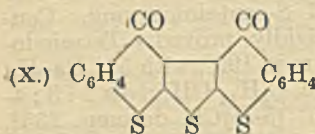
Natural coumarins. XXIII. Xanthotoxol, a new natural substance from *Angelica* seeds and the total synthesis of xanthotoxol and imperatorin. E. SPÄTH and F. VIERHAPPER (Ber., 1937, 70, [B], 248—250).—Considerable amounts of imperatorin and small quantities of bergapten are present in the seeds. The latter are extracted with Et_2O and the phenolic compounds removed from the extract with KOH . The alkaline solution is acidified and extracted with Et_2O and the extract is exhausted with hot H_2O . After removal of the bulk of the fatty acids by boiling the aq. solution, the phenols are removed and distilled in a vac., thereby giving xanthotoxol (I), m.p. 251—252°, identical with that derived from imperatorin and methylated to xanthotoxin. (I) is also obtained by dehydrogenation (Pd-sponge at 170°) of synthetic 4' : 5'-dihydroxanthotoxol (A., 1936, 733). Since (I) is alkylated by isoprene hydrobromide to imperatorin (II) the synthesis of (I) supplies the missing link in the complete synthesis of (II). H. W.

Thiophen series. XXXIII. Iodine derivatives of thiophen and their reaction with thio-salicylic acid. W. STEINKOPF, H. F. SCHMITT, and H. FIEDLER. XXXIV. Iodine derivatives of 2-methylthiophen. W. STEINKOPF and W. HANSKE. XXXV. $\alpha\alpha\alpha$ -Tetrathienyl. W. STEINKOPF, H. J. VON PETERSDORFF, and R. GORDING (Annalen, 1937, 527, 237—263, 264—271, 272—278; cf. A., 1936, 619).—XXXIII. Various iodothiophens are prepared. The greater reactivity of atoms (including H) and groups in the α - as compared with the β -position is demonstrated. Iodo- but not bromo-thiophens condense with $o\text{-}SH \cdot C_6H_4 \cdot CO_2H$ (I) and lead to polycyclic systems of >1 S-containing ring. Substitutions assigned are rigidly proved. Tetraiodothiophen (modified prep.), m.p. 199°, with 5% Na-Hg in moist dioxan or with $Na \cdot C_5H_{11} \cdot OH$ gives 2 : 3 : 4-triiodothiophen, m.p. 116° (5-HgCl, decomp. 235°, and 5- NO_2 -derivative, m.p. 203—204°, but with Al and a little $HgCl_2$ in moist Et_2O - $EtOH$ yields 3-iodo- (II), b.p. 68°/12 mm., m.p. -13.4° [2-HgCl- (III), m.p. 138—139°, and 2 : 5-(HgCl)₂-derivative, decomp. 245—247°], and 3 : 4-di-iodo-thiophen (IV), b.p. 142—143°/12 mm., m.p. 4.5° [2 : 5-(HgCl)₂, m.p. 165°, 2-HgCl-, m.p. 178—180°, 2- NO_2 - (V), m.p. 163—164°, and 2 : 5-(NO_2)₂-derivative, m.p. 148—151°]. (IV) with $MgEtBr$ gives a 48% yield of (II) and with $MgEtBr \cdot CO_2$ yields 3-iodothiophen-4-carboxylic acid, m.p. 169—170° (2 : 5- Br_2 -derivative, m.p. 182°). With $H_2SO_4 \cdot HNO_3$ (V) gives two 3-iododinitrothiophens, m.p. 187—188° and 119—120°, respectively. With I and HgO in C_6H_6 (II) gives 2 : 3 : 5-tri-iodothiophen, m.p. 87—88°. (III) and I-KI give 2 : 3-di-iodothiophen, b.p. 138.5°/12 mm., m.p. -10° (5-HgCl-, decomp. 228°, and 5- NO_2 -derivative, m.p.

79—80°), converted by $\text{MgEtBr} \cdot \text{CO}_2$ into 3-iodothiophen-2-carboxylic acid, m.p. 193—195° (decomp.) (4:5- Br_2 -derivative, m.p. 267—268°), and by $\text{Br} \cdot \text{CS}_2$ into 2:3:5-tribromo-4-iodothiophen, m.p. 111—112°, or 2:5-dibromo-3:4-di-iodothiophen, m.p. 141—142° (also obtained from tetraiodothiophen). 2-Iodothiophen, (I), K_2CO_3 , and a trace of $\text{Cu}(\text{OAc})_2$ in $\text{C}_5\text{H}_{11}\text{OH}$ at 135—145° give 2-thienyl o-carboxyphenyl sulphide (VI), m.p. 195—197° [amide, m.p. 198—201°, resistant to Hofmann degradation; s-di-(2-thienyl o-carboxyphenyl sulphide) hydrazide, m.p. 208—211°], the hydrazide, m.p. 145—147°, of which gives the impure azide, decomp. from 85°, and thence in various ways the stable carbimide, m.p. 184—186°, converted by H_2O at 200—210° into 2-thienyl o-aminophenyl sulphide, m.p. 194—196° (diazotises and couples normally). (VI) is dehydrated by conc. H_2SO_4 at 90—95° or by PCl_5 in hot C_6H_6 to give thiopheno- $\alpha\beta$ -thiochromone [thiopheno-2':3':2:3-benzthio-1:4-pyrone] (VII), m.p. 157—158°, converted by Zn dust and $\text{AcOH} \cdot \text{H}_2\text{SO}_4$ into bithiopheno- $\alpha\beta$ -

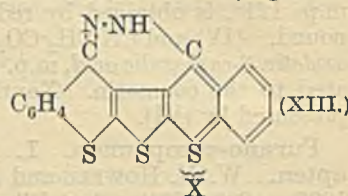
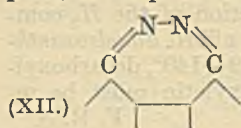


thiochromylene (VIII), m.p. 320—322° (decomp.). 2:5-Di-iodothiophen gives similarly 2:5-di-(o-carboxyphenylthiol)thiophen (IX), decomp. 300—305° [dichloride, m.p. 155.5—157.5° after sintering; diamide, m.p. 278—279° (decomp.)], converted by fuming HNO_3 into 3:4-dinitrothiophen 2:5-di-(o-carboxyphenyl) disulphoxide, decomp. 217.5°, which with SOCl_2 , followed by $\text{NH}_3 \cdot \text{C}_6\text{H}_6$, gives 3:4-dinitro-2:5-di-(o-carbonamidophenylthiol)thiophen, m.p. 204—205° (decomp.). PCl_5 in hot C_6H_6 chlorinates (IX) to give 3-chloro-2:5-di-(o-carboxyphenylthiol)thiophen, m.p. 311° (decomp.) (dichloride, m.p. 154.5—156°; 4- NO_2 -derivative, decomp. 220—225°). (IX) is dehydrated by conc. H_2SO_4 to $\alpha\beta\alpha'\beta'$ -thiophenobisthiochromone [bis(benzthio-1:4-pyrone-2:3)-2':3':5':4'-thiophen] (X), yellow, m.p. 273° after sintering

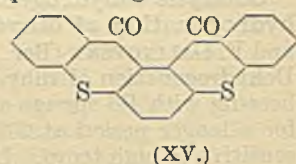
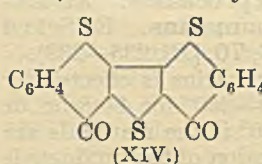


[(? 3:6-)(NO_2)₂-derivative, decomp. from 370°], converted by $\text{NHPh} \cdot \text{NH}_2$ in AcOH into a phenylhydrazone, decomp. 222°, which is brown-yellow in neutral but blue-green in acid solution, gives a nearly black picrate, m.p. 237—239°, a green pentabromide, and green hydrochloride, m.p. 294°, and thus resembles the tetra-arylhydrazones. Other similar phenylhydrazones do not behave thus. With N_2H_4 (X) gives the bluish-violet azo-compound (XI) (dihydro- $\alpha\beta\alpha'\beta'$ -thiophenobisthiochromone) (10%), m.p. 298—299°, red $\alpha\beta\alpha'\beta'$ -thiophenobisthiochromoneazine (XII) (2.5%), m.p. 297°, and a trace of a substance, $\text{C}_{36}\text{H}_{20}\text{N}_2\text{S}_6$, m.p. 290.5°. (XII) gives blue solutions in acid and a blue sulphate and may exist as (XIII). (IV) and (I) lead to 3:4-di-(o-carboxyphenylthiol)thiophen, m.p. 282—283° after sintering, converted by PCl_5 in C_6H_6

into 2:5-dichloro-3:4-di-(o-carboxyphenylthiol)thiophen, decomp. 321°, sublimes at about 250°/high vac.



(dichloride, m.p. 166—168°), by fuming HNO_3 into the disulphoxide, decomp. 262°, and by conc. H_2SO_4 at 90° into $\beta\alpha\beta'\alpha'$ -thiophenobisthiochromone [bis(benzthio-1:4-pyrone-3:2)-2':3':5':4'-thiophen] (XIV) (poor yield), m.p. 359—360°, sublimes at 240—260°/high vac. Tetraiodothiophen gives 2:3:4:5-tetra-(o-carboxyphenylthiol)thiophen, decomp. 320—322°; 5:5'-di-iodo-2:2'-dithienyl gives 5:5'-di-(o-carboxyphenylthiol)-2:2'-dithienyl, m.p. 299—300°; p- $\text{C}_6\text{H}_4\text{I}_2$ gives p-di-(o-carboxyphenylthiol)benzene, m.p. 305—307°, converted by H_2SO_4 into ang.-benzobisthio-

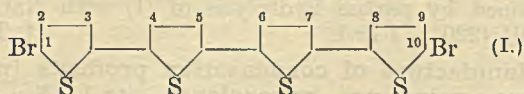


chromone (XV), m.p. 285—285.5°, the orange internal azine, m.p. 348—349°, of which gives a bluish-black, cryst. hydrochloride and a red sulphate, probably similar in structure to (XIII). 2-Iodothiophen-5-carboxylic acid and Br give 4:5-dibromothiophen-2-carboxylic acid, m.p. 226—227°. The following data are new: 2-iodo-, m.p. -40° to -41°, b.p. 73°/15 mm., 2:4-, m.p. -32.5° to -27.5°, and 2:3-dibromothiophen, m.p. -17.5°; 3:5-dibromo-2-methylthiophen, m.p. -15.2°. The chloride of (VI) reacts with NaN_3 only in PhNO_2 at 150—170°. Interaction of 2:2'-di-iododithienyl-5:5'-dimercurichloride with (I) causes loss of Hg.

XXXIV. 2-Methylthiophen gives only a 62% yield of 3:4:5-(HgOAc)₃-derivative, decomp. >200° [whence the (HgCl)₃-derivative, decomp. >240°, is readily obtained], but when I is added gradually to its solution with $\text{Hg}(\text{OAc})_2$ in hot AcOH gives a 53% yield of 3:4:5-tri-iodo-2-methylthiophen (I), m.p. 100—101.5°. The isolated (HgOAc)₃- and (HgCl)₃-derivatives give only a 30% yield with 3:5- and 4:5-di-iodo- and 5-iodo-2-methylthiophen, b.p. 88.8—89.3°/14 mm., m.p. -28° to -25.6°. (I) and MgMeBr give 3:4-di-iodo-, m.p. 44—45° (5- HgCl -derivative, m.p. 216.5—218°), and 4-iodo-2-methylthiophen (II), b.p. 90—91.8°/12 mm., m.p. -6.5° to -5.5°. (II) and $\text{MgMeBr} \cdot \text{CO}_2$ give 2-methylthiophen-4-carboxylic acid, m.p. 131—132°, and the 5- HgCl -derivative, m.p. 201.5—203°, of (II) with I-KI gives 4:5-di-iodo-2-methylthiophen, m.p. 37.5—38.5°. 3-Bromo-2-methylthiophen and $\text{MgMeBr} \cdot \text{I}$ yield 3-iodo-2-methylthiophen, b.p. 78—79°/10 mm., m.p. -17° to -15.6°, the 5- HgCl -derivative, decomp. >200°, of which with I-KI gives 3:5-di-iodo-2-methylthiophen, b.p. 103—105°/2 mm., m.p. 6.5—8°. (I) and $\text{MgMeBr} \cdot \text{CO}_2$ give 4-iodo-, m.p. 186—188°, and 3:4-di-iodo-2-methylthiophen-5-carboxylic acid, m.p. 236° (decomp.).

(I) is obtained from 2-methylthiophen-5-carboxylic acid by way of the $(\text{HgOAc})_2$ -derivative.

XXXV. 5 : 5'-Dibromo-2 : 2'-dithienyl and $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ give a poor yield of 1 : 10-dibromo- $\alpha\alpha$ -tetrathienyl (I), m.p. 248°, converted by an excess of Br into decabromotetrathienyl (II), m.p. 326—328°.



2 : 3-Dibromothiophen and MgEtBr , followed by CuCl_2 , give 3 : 3'-dibromodithienyl, m.p. 96—97°, converted by Br into 3 : 5 : 3' : 5'-tetrabromodithienyl, m.p. 139—140°, and by $\text{Hg}(\text{OAc})_2\text{-AcOH-KCl-I-KI}$ into 3 : 3'-dibromo-4 : 5 : 4' : 5'-tetraiodo-2 : 2'-dithienyl, m.p. 273—274°. A mixture of 2-iodo- and 2 : 5-di-iodo-thiophen and Cu-bronze at 195—200° give a little $\alpha\alpha$ -tetrathienyl, m.p. 208—209°, sublimes at 160—175°/high vac., yellow, converted by Br into (II) and obtained also from 5 : 5'-di-iodo-2 : 2'-dithienyl, 2-iodothiophen, and Cu-bronze. 5-Iodo-2-phenylthiophen (from the 5-HgCl-derivative and I-KI) with MgEtBr-CuCl_2 gives a little 5 : 5'-diphenyl-2 : 2'-dithienyl, m.p. 237°, yellow, obtained also from 5-bromo-2-phenylthiophen, m.p. 85—86° (prep. from 2-phenylthiophen and BrCN at 30—40°). 2 : 5-Di-iodothiophen and H_2SO_4 give only 2 : 3 : 5-tri- and tetra-iodothiophen. The colour of the polythienyl compounds is due to conjugation and shows that thiophen is less aromatic than C_6H_6 .

R. S. C.

3- β -Hydroxyethylproline. V. PRELOG and E. CERKOVNIKOV (Coll. Czech. Chem. Comm., 1937, 9, 22—27).—Tetrahydropyran-4-aldehyde with aq. $\text{KCN-NH}_4\text{Cl}$ (60°, 6 hr.) affords α -amino- β -4-tetrahydropyranylpropionic acid (urethane, m.p. 184.5°), which with HBr (100°, 8 hr.) yields 8-bromo- α -amino- β -(β' -bromoethyl)valeric acid, m.p. 100—101° [picrolonate, m.p. 183° (decomp.)], the lactone of which with Ag_2O gives the α -lactone (hydrochloride, m.p. 260—262°) of 3- β -hydroxyethylproline (Na and Ag salts); the Ag salt of the lactone hydrochloride with MeI (1 hr, 50°) affords 1-methyl-3- β -hydroxyethylpyrrolidine- α -lactone methochloride, m.p. 230° (decomp.).

F. N. W.

Electrolytic reduction of maleimide and pyrrolidine. B. SAKURAI (Bull. Chem. Soc. Japan, 1937, 12, 8—11).—Electrolytic reduction of maleimide with a Pb or Cu cathode in 10% H_2SO_4 containing a Ni catalyst gives succinimide (80% yield), but with a Zn-Hg cathode in 50% H_2SO_4 preliminary hydrolysis to NH_3 and maleic acid occurs, and the latter is reduced to $(\text{CH}_2\text{CO}_2\text{H})_2$. Reduction of pyrrolidine with Pb cathode-10% H_2SO_4 -Ni gives some pyrrolidine, isolated as its aurichloride.

J. W. B.

Syntheses in the homoneurin series. IV. Bromo-derivatives of pyridine homoneurin. E. MACOVSKI and E. RAMONTIANU (Bul. Soc. Stiinte Cluj, 1935, 8, 272—278; Chem. Zentr., 1936, i, 2353).— $\text{C}_5\text{H}_5\text{N}$ and $\text{CH}_2\text{:CH-CH}_2\text{Br}$ in C_6H_6 afford allylpyridinium bromide (pyridine homoneurin bromide) (I), m.p. 95—96°, which with 2 Br in EtOH yields $\beta\gamma$ -dibromopropylpyridinium bromide (II), m.p. 142—143°; this with 2 Br or (I) with 4 Br yields $\beta\gamma$ -dibromo-

propylpyridinium dibromobromide, m.p. 77—79°. (II) with KI yields $\beta\gamma$ -dibromopropylpyridinium iodide, b.p. 115—118° (decomp.), which with 2 Br yields $\beta\gamma$ -dibromopropylpyridinium dibromiodide, m.p. 92—94°.

H. N. R.

Onium compounds. XVI. Quaternary derivation of pyridyl ethers. R. R. RENSCHAW and R. C. CONN (J. Amer. Chem. Soc., 1937, 59, 297—301).—The following 2-aryloxy-pyridines are prepared from 2-bromopyridine (I) (1 mol.), ArOH (2 mols.), and anhyd. K_2CO_3 (1 mol.) at 200—210° (bath): 2-phenoxo-, b.p. 134—135°/11 mm. [methiodide (II), m.p. 174—175°; ethiodide, m.p. 150.5—151.5°], 2-o-tolyl-oxy-, b.p. 156—158°/21 mm. [methiodide, m.p. 186—186.2° (decomp.); ethiodide, m.p. 122—124°], 2-m-tolyl-oxy-, b.p. 164—166°/20 mm. (methiodide, m.p. 145—146.5°; ethiodide, m.p. 126—126.5°), 2-p-tolyl-oxy-, b.p. 171.5—172.5°/22 mm. (methiodide, m.p. 149—150°), and 2-2'-methyl-5'-isopropylphenoxy-, b.p. 133—134°/2 mm. (methiodide, m.p. 134—135°), -pyridine. Resorcinol di-2-pyridyl ether, b.p. 183—185°/3 mm., m.p. 154—156°, is similarly prepared. 2-Benzyl-oxy-pyridine [from (I) and $\text{CH}_2\text{Ph-OH-CH}_2\text{Ph-ONa}$] has b.p. 162—164°/20 mm. The following are prepared from 4-pyridylpyridinium dichloride and the appropriate ROH-NaOR by Koenigs and Greiner's method (A., 1931, 850): 4-methoxy-, b.p. 95—96°/31 mm. [picrate, m.p. 171—172°; methiodide, m.p. 145° (decomp.)], 4-n-butoxy-, b.p. 129—131°/25 mm. (methiodide, m.p. 74—75°), 4-phenoxy-, b.p. 157—158°/21 mm. [methiodide (III), m.p. 227.5—228.5°; ethiodide, m.p. 110.5—111°], 4-o-tolyl-oxy-, b.p. 161—162°/19 mm. (methiodide, m.p. 163—164°; ethiodide, m.p. 148°), 4-m-tolyl-oxy-, b.p. 124—126°/4 mm. (methiodide, m.p. 157—158°; ethiodide, m.p. 128°), and 4-p-tolyl-oxy-pyridine, b.p. 166—167°/22 mm. (methiodide, m.p. 163°; ethiodide, m.p. 126—126.5°; β -phenoxyethobromide, m.p. 129—130°). 3-Phenoxy-pyridine, b.p. 147—149°/17 mm. [methiodide (IV), m.p. 82.5—84°; ethiodide, m.p. 136—137°], is prepared from 3-iodo-pyridine and NaOPh in PhOH and from 3-hydroxy-pyridine, its K salt, and PhBr in presence of Cu-bronze. Reduction (H_2 , PtO_2) of (II) (in EtOH) and (III) (in H_2O), followed by treatment with MeI and $\text{Ba}(\text{OH})_2$, gives dimethylpiperidinium iodide, whilst (IV) similarly affords 3-phenoxydimethylpiperidinium iodide, m.p. 177—178° (some fission occurs when a large amount of catalyst is used). The aromatic nature of 3-substituted pyridines and the lability of the 2- and 4-derivatives is emphasised. N-4'-Pyridyl-4-pyridone (Arndt, A., 1932, 283) [aurichloride, m.p. 218—219°; platinichloride, m.p. >300°; dihydrochloride, m.p. 238° (decomp.)] and AlKI in C_6H_6 at 80° give the N'-methiodide, m.p. 238—238.5°, and N'-ethiodide (+ H_2O), m.p. 134—135°. All b.p. and m.p. are corr.

H. B.

Halogenated pyridinecarboxylic acids. R. GRAF (J. pr. Chem., 1937, [ii], 148, 13—23).—3 : 5-Dichloro-4-hydroxypicolinic acid when heated with $\text{PCl}_5\text{-POCl}_3$ gives 3 : 4 : 5-trichloropyridine-2-carboxylic acid (chloride, b.p. 135—136°/12 mm., m.p. 24—25°; Et, m.p. 34—35° and Ph, m.p. 93—94°, esters), converted by heating with HI-red P into

3 : 5-dichloropyridine (I), 3 : 5-dichloro-5-iodopyridine, m.p. 183°, and 3 : 5-dichloropyridine-2-carboxylic acid, m.p. 152° (*Me* ester, m.p. 82°), readily decarboxylated to (I). 3 : 5-Dibromo-4-hydroxypicolinic acid with PCl_5 -MeOH gives *Me* 4-chloro-3 : 5-dibromopicolinate, m.p. 105°, hydrolysed to the free acid, m.p. 163—164° (*amide*, m.p. 194°), converted by heating with HI into 3 : 5-dibromopyridine-2-carboxylic acid, m.p. 144—145° (*amide*, m.p. 172°; *Me*, m.p. 96—97°, and *Ph*, m.p. 65°, esters). Similarly from 3 : 5-diiodo-4-hydroxypicolinic acid and PCl_5 at 150° is obtained *Me* 4-chloro-3 : 5-diiodopyridine-2-carboxylate, m.p. 106°, from which the acid could not be obtained by hydrolysis. 4-Chloro-6-hydroxypicolinic acid with Cl_2 -*N*-KOH gives the 3 : 4 : 5- Cl_3 -derivative, m.p. 238° (decomp.) (*Me* ester, m.p. 212—214°), in which the 6-OH could not be replaced by Cl. 3 : 5-Diiodochelidamic acid and PCl_5 -MeOH give *Me* 4-chloro-3 : 5-diiodopyridine-2 : 6-dicarboxylate, m.p. 144°. When heated with HI-red P 4-chloro- gives 4-iodo-pyridine-2 : 6-dicarboxylic acid, m.p. 208° (decomp.) (*Me*₂ ester, m.p. 168°; *diamide*, m.p. 297°). 3-Aminopicolinic acid is converted by diazotisation and I into 3-iodopyridine-2-carboxylic acid (II), m.p. 137—138°, isolated as a *basic hydriodide*, 4(II),HI, m.p. 142° (decomp.), converted by crystallisation from conc. HI into the *hydriodide*, (II),HI, m.p. 188°. The chloride of tetrachloroisonicotinic acid is converted by HI into 3 : 5-dichloropyridine-4-carboxylic acid. J. W. B.

Structure of isatin. I. E. G. COX, T. H. GOODWIN, and A. I. WAGSTAFF (Proc. Roy. Soc., 1936, A, 157, 399—411).—X-Ray and optical data for cryst. isatin (I) and various related compounds are given. The cell dimensions of (I) do not give any indication of the mol. arrangement. The mols. appear to be disposed in parallel layers so that the distance between C_1N of one mol. and C_2O of its neighbour is about 2.8 Å, i.e., some form of co-ordination (possible types discussed) occurs. The structure of (I) is probably intermediate between the lactam and lactim forms. *N*-Methylisatin (II) exists in α -, β -, and (probably) γ -modifications; the structures of the α - and β -forms appear to be very complex and are not simply related to those of (I) or *O*-methylisatin (III). The conversion of (III) into methylisatoid (IV) in the solid state in air is followed by X-ray methods; the results confirm that (IV) is $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_2$ (cf. von Baeyer, A., 1883, 201; Heller and Benade, A., 1922, i, 582; Hantzsch, A., 1922, i, 1177). (IV) does not appear to be a 1 : 1-compound of (I) and (II). The production of (I) during evaporation of a solution (EtOH) of (III) is explained thus : (III) \rightarrow *o*- $\text{NH}_2\text{C}_6\text{H}_4\text{CO}\cdot\text{CO}_2\text{Me}$ (or H) \rightarrow (I) + MeOH (or H_2O). The X-ray powder photograph of 3-hydroxy-2-quinolone resembles that of (I), indicating a similarity in mol. arrangement. H. B.

3-Hydroxy-1 : 2 : 3 : 4-tetrahydroquinoline derivatives.—See B., 1937, 219.

Synthesis of 2 : 4-diarylaminoquinoline derivatives. K. DZIEWOŃSKI and W. DYMEK (Roczn. Chem., 1936, 16, 479—485).—Diphenylacetamidine and PhNCS (220°; 4 hr.) yield 2 : 4-dianilinoquinoline (I), m.p. 169—170° (lit., 145°) [*hydrochloride*, m.p.

306°; *picrate*, m.p. 258—259°; 2 : 4-*N*-(NO)₂-derivative, m.p. 150° (decomp.); *N*-Ac derivative, m.p. 173°]. (I) is also prepared from 2 : 4-dichloroquinoline and NH_2Ph (5 min. at the b.p.). A mixture of 4-anilino-2-hydroxy- and 2-anilino-4-hydroxyquinoline, m.p. 325° (*hydrochloride*, m.p. 251°), is obtained by partial hydrolysis of (I) with NaOH-EtOH (220°; 4 hr.). R. T.

Manufacture of condensation products [pyridines, quinolines, pyrazolones, etc.].—See B., 1937, 217.

Manufacture of condensation products (pyrroles, indoles, carbazoles).—See B., 1937, 219.

Hydroxy carbazolemonosulphonic acids.—See B., 1937, 220.

Oxidising action of selenium dioxide. II. L. MONTI (Atti R. Accad. Lincei, 1936, [vi], 24, 145—146; cf., A., 1934, 664).—5-Methylacridine is oxidised by SeO_2 in AcOH to acridine-5-aldehyde. O. J. W.

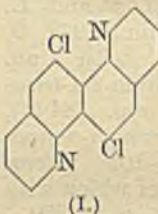
(A) Reactions of 1- and 2-nitronaphthalene and 1 : 5-dinitronaphthalene with glycerol and hydrochloric acid. H. KUCZYŃSKI, E. SUCHARDA, and A. SURMIŃSKI. (B) Reactions of 5-, 6-, 7-, and 8-nitroquinoline with glycerol and hydrochloric acid. H. KUCZYŃSKI and E. SUCHARDA. (C) Reactions of *o*- and *p*-nitrotoluene and *o*-nitrophenol with glycerol and hydrochloric acid. T. MAZOŃSKI, T. MIELECKI, and E. SUCHARDA (Roczn. Chem., 1936, 16, 509—512, 513—518, 519—523).—

(A) 1- $\text{C}_{10}\text{H}_7\text{NO}_2$, glycerol, and conc. HCl (160—170°; 20 hr.) yield 6-chloro- α -naphthoquinoline, m.p. 101° (*picrate*, m.p. 240°), also prepared by the Skraup synthesis from 4 : 1- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{NH}_2$. Under similar conditions, 2- $\text{C}_{10}\text{H}_7\text{NO}_2$ yields β -naphthoquinoline, and 1 : 5- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$ gives 4 : 8-dichloro-1 : 5-naphthodiquinoline (I), m.p. 269—271° (*hydrochloride*; *nitrate*; *sulphate*).

(B) Under the above conditions, 10-chloro-*m*-phenanthroline, m.p. 124.5° [*nitrate*, m.p. 197° (decomp.); *hydrochloride*, m.p. 239° (decomp.); *picrate*, m.p. 229° (decomp.); *dichromate*, m.p. 175—177° (decomp.)], is obtained from 5-, 5-chloro- α -phenanthroline, m.p. 123° [*hydrochloride*, m.p. 266°; *picrate*, m.p. 215—216° (decomp.)], from 8-, ψ -phenanthroline from 6-, and *m*-phenanthroline from 7-nitropyridine.

(C) The chief products of the above reaction with *o*- or *p*-nitrotoluene are 6-chloro-8-, m.p. 65.5°, or 8-chloro-6-methylquinoline, m.p. 62.5° (*picrate*, m.p. 213°), together with 6-methylquinoline, whilst *o*-nitrophenol gives a mixture of 8-hydroxy- and 6-chloro-8-hydroxyquinoline, m.p. 124°. R. T.

Synthetic nucleosides. 1-Glycosidouracils. G. E. HILBERT (J. Amer. Chem. Soc., 1937, 59, 330—333; cf. A., 1931, 100).—Acetobromo-*d*-xylose (I) and 2 : 4-diethoxypyrimidine (II) at 65°/18 hr. give 2-keto-4-ethoxy-1-triacetyl-*d*-xylosido-1 : 2-di-hydropyrimidine, m.p. 218°, $[\alpha]_D^{25} + 58.4^\circ$ in CHCl_3 , deacetylated (EtOH- NH_3) to the 1-*d*-xylosido-derivative, m.p. 208° (sinters at 206°), $[\alpha]_D^{25} + 47.9^\circ$ in H_2O , and hydrolysed (MeOH-HCl) to 1-*d*-xylosido-

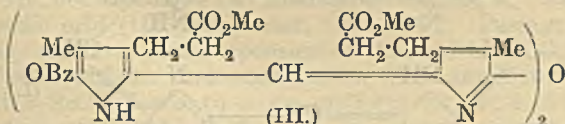


(I)

uracil, m.p. 245° (sinters at 243°), $[\alpha]_D^{25} +21.8^\circ$ in H_2O . 2-Keto-4-ethoxy-1-tetra-acetyl-d-galactosido-, m.p. 159° (sinters at 156°), $[\alpha]_D^{25} +59.2^\circ$ in $CHCl_3$, and -1-triacetyl-1-arabinosido-, dimorphous, m.p. 157° and 167.5° (stable), $[\alpha]_D^{25} +108.8^\circ$ in $CHCl_3$, -1:2-dihydropyrimidines, similarly prepared from (II) and acetobromo-d-galactose (III) and -l-arabinose, respectively, are similarly hydrolysed to 1-d-galactosido-, m.p. 250–251°, $[\alpha]_D^{25} +59.9^\circ$ in H_2O , and 1-l-arabinosido-, m.p. 251–252°, $[\alpha]_D^{25} +88.2^\circ$ in H_2O , -uracil, respectively. A cryst. mannosido-derivative could not be isolated from the syrup obtained from (II) and acetobromo-d-mannose (IV). By-products isolable in the reactions between (II) and the acetobromoglycosides are 2-keto-4-ethoxy-1:2-dihydropyrimidine [from (III) and (IV)] and its 1-Et derivative (V), m.p. 88° [from (I), (IV), and acetobromo-d-glucose], which probably results owing to the intermediate formation of EtBr. (V) is hydrolysed (conc. HCl) to 1-ethyluracil, m.p. 147.5°. All m.p. are corr. H. B.

Synthesis of flavanthrene starting with benzene. V. KRPELKA and R. ŠTEFEC (Coll. Czech. Chem. Comm., 1937, 9, 29–34).—2:2'-Diaminodiphenyl (modified prep.) with $o-C_6H_4(CO)_2O$ gives 2:2'-diphthalimidodiphenyl, m.p. 209°, which condenses ($AlCl_3-NaCl$; 2 hr. 160° rising to 210° followed by 6 hr. 210° rising to 235°) to form flavanthrene (I) and an intermediate compound, m.p. about 380°, which with H_2SO_4 at 250°, or $AlCl_3$ at 210–230°, affords (I). F. N. W.

Pentduopent reaction. I. H. FISCHER and A. MÜLLER (Z. physiol. Chem., 1937, 246, 43–58).—Pentduopent (I) (absorption band at about 525 mμ), first observed by the reduction of pathological urine by $(NH_4)_2S$ and Sn or sugar in an alkaline medium, is obtained from many tetranuclear pyrrole pigments and pyromethenes but not from normal urine, brown urine pigment, hæmatic acid, methylethylmaleinimide, all investigated pyrroles, hydroxypyrroles, and dipyrrol ethers and pyroketones, and certain methenes. It is therefore a group reaction. Oxidation of 5:5'-dibromo-4:4'-dimethylpyromethene-3:3'-dipropionic acid hydrobromide (II) with H_2O_2 in aq. NH_3 gives (I), which could not be obtained cryst. or as a cryst. derivative but is free from halogen, retains all the original N atoms, and can be esterified by CH_2N_2 . It is also obtained by the action of air on (II) in aq. NH_3 . A very similar (I) results from the oxidation of 5:5'-dicarboxy-4:4'-dimethylpyromethene-3:3'-dipropionic acid. This does not react with $NH_2 \cdot CO \cdot NH \cdot NH_2$, $NHPh \cdot NH_2$, N_2H_4 , or NH_2OH , and although reaction takes place it does not give cryst. derivatives with Ac_2O , $BzCl$, $PhSO_2Cl$, or $C_{10}H_7 \cdot SO_2Cl$. The NH_4 salt with Me_2SO_4 gives a



non-cryst. ester, transformed by $BzCl$ in presence of $MgCO_3$ into the compound (III), m.p. 193°, which gives a bluish-green Ehrlich reaction with an absorption spectrum similar to that of neoxanthobilirubin

acid. Reasons are advanced for assigning the 2:2'-dihydroxymethene structure to (I). Long keeping or heating of (I) with $NaOH$ causes evolution of NH_3 and disappearance of the red colour; hæmatic anhydride is obtained from the solution. $Na-Hg$ in H_2O causes disappearance of the colour and production of a red Ehrlich reaction. Towards $HI-AcOH$ (I) is relatively stable but prolonged action of the boiling reagent after addition of PH_4I leads to the formation of NH_4I and succinic acid. The possible structure of (I) and its formation from blood pigments are discussed. H. W.

Complex piperazine-metal sulphates. R. RIPAN-TILICI (Ber., 1937, 70, [B], 401–407).—Evaporation of aq. solutions of the respective metallic sulphates and piperazine sulphate until crystallisation occurs on cooling gives salts $RSO_4 \cdot H_2SO_4 \cdot X \cdot 6H_2O$ in which $R = Zn, Mg, Cd, Fe, Ni, Co, Mn$, or Cu and $X =$ piperazine. The Mg, Ni , and Cd salts form one series and the Co, Zn , and Mn salts a second series of isomorphous compounds to neither of which the Cu and Fe salts can be assigned. The feebly complex character of the substances is shown by their complete dissociation in H_2O . The presence of a metal hydrate complex $[R(H_2O)_6]^{+}$ is established by the correspondence of their colour with that of the simple sulphates and by their transition by $(CH_3 \cdot NH_2)_2$ at 18–20° into the compounds $[R en_3]_2 \cdot H_2SO_4 \cdot X$, in which $R = Ni, Co, Cu$, or Cd . Similarly, the salts $[Cu(NH_3)_4]SO_4 \cdot H_2SO_4 \cdot X$ and $[Ni(C_5H_5N)_4(H_2O)_2]SO_4 \cdot H_2SO_4 \cdot X$ are obtained. H. W.

Structure of indazoles. K. VON AUWERS [with R. HÜGEL and O. UNGEMACH] (Annalen, 1937, 527, 291–298).—Presence of 3-substituents does not alter the benzenoid structure of 1- nor the *o*-quinonoid structure of 2-derivatives of indazole, as disclosed by *n*. 3-Chloroindazole, m.p. 147–148°, is obtained in 75–80% yield from indazole and $NaOCl$; alkylation gives a mixture of 1- and 2-derivatives, separable by the picrates. The following are new: 3-chloro-1-, b.p. 128–129°/10 mm. (picrate, m.p. 86°), and -2-methyl-, m.p. 53–54°, b.p. 120–121°/10 mm. (picrate, m.p. 129–131°), -1-, b.p. 129°/10 mm. (picrate, m.p. 65–66°), and -2-ethyl-, b.p. 123–124°/9 mm. (picrate, m.p. 124–125°), -indazole and 1-acetylindazole, m.p. 65° (lit. 67°). R. S. C.

Luminol. W. LANGENBECK and U. RUGE (Ber., 1937, 70, [B], 367–369).—A solution of 0.1 g. of luminol (3-aminophthalhydrazide hydrochloride) and 2 mgm. of cryst. hæmin in 1% Na_2CO_3 (100 c.c.) gives a distinct chemiluminescence with 0.012×10^{-6} g. of H_2O_2 . The reaction is also given by BzO_2H and $(NH_4)_2S_2O_8$ owing to hydrolytic formation of H_2O_2 . The formation of H_2O_2 during the autoxidation of dioxindole and 3-aminodioxindole can be detected by this method but not by the usual reagents. H. W.

Cyclic quinolinic acid hydrazide and related compounds. K. GLEU and K. WACKERNAGEL (J. pr. Chem., 1937, [ii], 148, 72–80).—Quinolinic acid anhydride with aq. N_2H_4 gives the hydrazide, m.p. 309° (hydrochloride, m.p. 309°); its 6-OH-derivative, decomp. >400°, is obtained similarly or from

$N_2H_4 \cdot H_2O$ and the appropriate Me ester. Halogenation of this Me ester, m.p. 158° , of 6-hydroxyquinolinic acid [anhydride, m.p. 245° (O-Ac derivative, m.p. 109°); imide, m.p. 334° (O-Ac derivative, m.p. 257°)] gives the 5-halogeno-derivative from which the hydrazides are prepared and thus are obtained 5-chloro-, m.p. 228° (decomp.) (Me ester, m.p. 163° ; hydrazide, decomp. $380-400^\circ$), 5-bromo-, m.p. 229° (decomp.) (Me ester, m.p. 182° ; hydrazide, decomp. $400-450^\circ$), and 5-iodo-, m.p. 235° (decomp.) (Me ester, m.p. 216° ; hydrazide, decomp. $420-450^\circ$), 6-hydroxyquinolinic acid. None of these hydrazides exhibits either fluorescence or chemiluminescence.

J. W. B.

[Polymeric indoles.] O. SCHMITZ-DUMONT and J. TER HORST (Ber., 1937, 70, [B], 182; cf. A., 1935, 502).—A correction of analytical data with reference to dinitrosoacetyltri-indole.

H. W.

Formation of dihydrazidines and dihydro-tetrazines from dithiocarbonic acids. H. WUYTS and (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1936, 45, 685-692).—The acids $R \cdot CS_2H$ ($R = Ph$, p - C_6H_4Me , α - $C_{10}H_7$) with N_2H_4 in EtOH yield thiohydrazides, converted by excess of N_2H_4 into dihydrazidines and 1:2:4:5-tetrazines. Arylthioaroylhydrazines $R \cdot CS \cdot NH \cdot NHR'$ (I) ($R = Ph$, $R' = Ph$ or p - C_6H_4Me) with N_2H_4 and S in EtOH afford a mixture of diphenyldihydrazidine (II) and diphenyldihydro-tetrazine (III), both oxidised to diphenyl-tetrazine. (I) ($R = p$ - C_6H_4Me , $R' = Ph$ or o - C_6H_4Me) similarly yields di- p -tolyl-dihydro-tetrazine, and di- p -tolyl-dihydrazidine, both oxidised to di- p -tolyl-tetrazine. Thiobenzamide with N_2H_4 and S in EtOH yields (II) and (III).

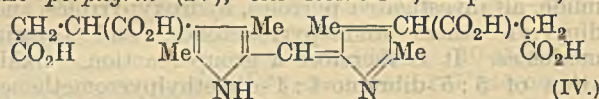
J. D. R.

Synthesis of mesobilirubin (mesobilirubin-IX α). W. SIEDEL (Z. physiol. Chem., 1937, 245, 257-275).—The Me ester of formylneoxanthobilirubin acid in MeOH gives, with $PtO_2 \cdot H_2$, the corresponding $OH \cdot CH_2$ compound (I), m.p. 192° (corr.), hydrolysed to the acid by KOH in MeOH. (I) with isoneoxanthobilirubin acid in $CHCl_3$ gives, on saturation with dry HCl, the dihydrochloride, m.p. 199° (corr.), of the Me_2 ester, m.p. 240.5° (corr.), of mesobilirubin-IX α , m.p. 321° (corr.), also obtained from glaucobilin-IX α by reduction with Zn and AcOH. Crystallographic data are given for some of these substances and for mesobilirubin-III α and -XIII α , their Me_2 esters, m.p. $255-256^\circ$ (corr.) and 278.5° (corr.), respectively, and the dihydrochlorides of the esters. A system of nomenclature for substances of the bilirubin type is proposed, the classification depending on the no. of double linkings in the bridges which join the rings. The nomenclature suggested by Lemberg (cf. A., 1936, 1150) is rejected.

W. McC.

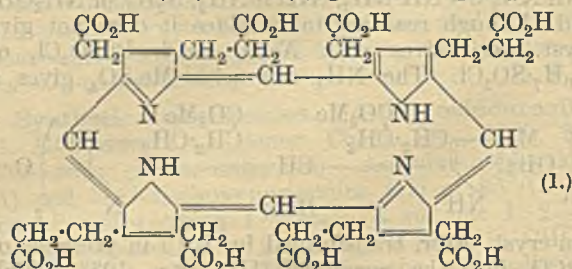
Porphyryns. XLI. Constitution of uro- and mussel-shell-porphyrin. Detection of uroporphyrin III in congenital porphyria. H. FISCHER and H. J. HOFMANN (Z. physiol. Chem., 1937, 246, 15-30).—Chromatographic analysis of natural uroporphyrin (Petty) (I), m.p. 286° , from MeOH- $CHCl_3$ by tale permits division into two fractions, m.p. $302-303^\circ$ and m.p. 261° after much blackening; the latter is identical with uroporphyrin

III. These observations increase the discrepancy between the m.p. of the natural and synthetic substances. The possibility that the latter material, obtained from an amorphous pyrromethene, contains impurity removable with difficulty is not supported by adsorption analysis and the following observations have been made in an attempt to explain the non-cryst. nature of the pyrromethene. Me_2 2:4-dimethylpyrrole-3-succinate could not be obtained from the corresponding acid (II) or by condensation of Et 2:4-dimethylpyrrole-5-carboxylate with $(iC \cdot CO_2Me)_2$. (II) and HCO_2H in AcOH at 100° afford 3:3':5:5'-tetramethylpyrromethene-4:4'-disuccinic acid, m.p. 221° (decomp.) after becoming discoloured at 205° , converted by CH_2N_2 in MeOH into the Me_4 ester, m.p. 151° . The action of AcOH-48% HBr on 2:4-dimethylpyrrole-5-aldehyde (III) and 2:4-dimethylpyrrole-3-succinic acid at 100° gives 3:3':5:5'-tetramethylpyrromethene hydrobromide, m.p. 251° (decomp.), by autocondensation of (III); this can be avoided if the reactants are heated for a very short time in AcOH at 100° , rapidly cooled, and the reagent added at room temp., whereby 3:3':5:5'-tetramethylpyrromethene-4'-succinic acid [hydrobromide, m.p. 229° (decomp.)] results. With 2:4-dimethyl-3-ethylpyrrole-5-aldehyde the autocondensation cannot be thus avoided and the product is 3:3':5:5'-tetramethyl-4:4'-diethylpyrromethene hydrobromide, incipient discoloration and decomp. 182° . Me_2 5-carbethoxy-2:4-dimethylpyrrole-3-succinate is converted by SO_2Cl_2 (3 mols.) followed by boiling H_2O into Me_2 5-carboxy-2-carbethoxy-3-methylpyrrole-4-succinate, m.p. 146° , converted by 15% NaOH at $170-180^\circ$ into 3-methylpyrrole-4-succinic acid, which is transformed by CH_2N_2 followed by distillation/15 mm. into the corresponding Me_2 ester, m.p. 58° , and a substance, $C_6H_9O_3N_2$, m.p. 171° , which does not contain OMe. The ester does not react with HCO_2H but in presence of $CH_2Cl \cdot OMe$ or $CHCl_2 \cdot OMe$ gives the porphyrin (IV), one isomeride, m.p. 317° , of



which is not identical with natural uroporphyrin, the succinic acid substitution in which is therefore doubtful. Oxidation of 2:5-dicarboxy-3-methylpyrrole-4-succinic acid by $CrO_3 \cdot H_2SO_4$ affords the compound (V) $\begin{array}{c} CO \cdot CMe \\ | \quad \quad \quad | \\ NH \quad \quad \quad CO \end{array} > C \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, m.p.

$195-196^\circ$ (marked decomp.), which with the carboxy-hæmatic acid (VI) from (I) gives strong depression



of the m.p. When heated at $180-220^\circ$ (VI) is partly unchanged and partly converted into hæmatic acid

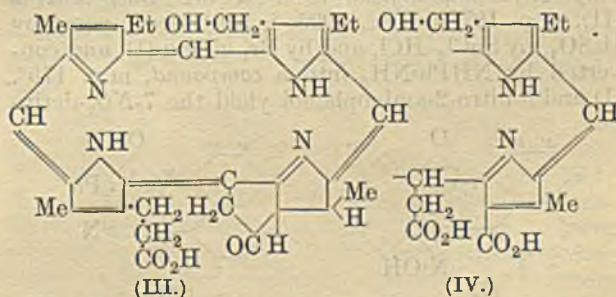
whereas below 200° (V) does not yield a sublimate. (VI) is converted at 260° into methylethylmaleimide, which is not formed from (V) under these conditions. The identity of uro- and mussel-shell-porphyrin is confirmed and the constitution shown is suggested for (I). H. W.

Imidoporphyrins. III. Complex salts of imidoporphyrins. H. FISCHER and A. MÜLLER (Annalen, 1937, 528, 1—8; cf. A., 1936, 1128).—The Me_4 ester (I) of di-imidocopropporphyrin (II) with $Fe(OAc)_2$ and NaCl in $AcOH-HCO_2H$ gives the *hæmin*, $C_{38}H_{42}O_8N_6FeCl$, which loses its Fe to N_2H_4-AcOH , but not to acid, not even to cold oleum. (I) and $MgBr \cdot OEt$ give the *phyllin*, m.p. 223°, of the Et_4 ester, which with 10% HCl readily gives the Et_4 ester, m.p. 229°, also obtained from (II) (obtained pure) and HCl-EtOH. 5:5'-Dibromo-4:4'-dimethyl-3:3'-diethylpyrrromethene hydrobromide and NH_3 in aq. C_5H_5N at 180° give an inseparable (?) mol. compound (0.415:0.585), m.p. 343°, of imido- and di-imido-porphyrin, which yields the pure *Fe* salt, m.p. >300°, of di-imidoetioporphyrin. 5:5'-Dibromo-3:3':4:4'-tetramethylpyrrromethene hydrobromide gives similarly imido-, m.p. 397° (block), and di-imido-octamethylpyrrrin, m.p. >350°, which form a (?) mol. compound (0.41:0.59), m.p. 445—447° (block). Spectroscopic data are given. R. S. C.

Porphyrins. XLII. Synthesis of a tetramethylporphintetra-acetic acid. Constitution of uroporphyrin. H. FISCHER and A. MÜLLER (Z. physiol. Chem., 1937, 246, 31—42).—The properties of synthetic porphyrinacetic acid are examined with reference to the constitution of uro- and conchoporphyrin (I). $CO(CH_2 \cdot CO_2Me)_2$ is treated with iso-amyl nitrite in presence of HCl-EtOH and the product with $CH_2Ac \cdot CO_2Et$ and Zn dust in $AcOH$ at 50—60°, thereby giving *Me* 5-carbomethoxy-3-carbethoxy-2-methylpyrrole-4-acetate, m.p. 136°; the corresponding acid, m.p. 241—243° (decomp.) after sublimation at 230° (Me_3 ester, m.p. 118°), could not be brominated. Et 3-aldehydo-2:4-dimethylpyrrole-5-carboxylate is condensed with $MeNO_2$ and NH_2Me in EtOH to *Et* 2:4-dimethyl-3- ω -nitrovinylpyrrole-5-carboxylate, which is reduced by Al-Hg in Et_2O to the corresponding oxime, m.p. 176°, dehydrated to Et 2:4-dimethyl-3-cyanomethylpyrrole-5-carboxylate (II), which is hydrolysed by boiling 10% KOH to 5-carboxy-2:4-dimethylpyrrole-3-acetic acid, m.p. about 121° (Me_2 ester, m.p. 136°). (II) in Et_2O is transformed by Br-AcOH into *Et* 4-methyl-2-bromomethyl-3-cyanomethylpyrrole-5-carboxylate, m.p. 184—185° (and a by-product, m.p. 223°), which loses CH_2O when boiled with H_2O and gives *Et_2* 4:4'-dimethyl-3:3'-dicyanomethylpyrrromethane-5:5'-dicarboxylate, m.p. 186°, hydrolysed to 5:5'-dicarboxy-4:4'-dimethylpyrrromethane-3:3'-diacetic acid (III) (Me_4 ester, m.p. 204°). Passage of dry air through a suspension of the acid in $HCO_2H-AcOH$ with 45° and esterification of the product with HCl-EtOH leads to a non-uniform Et_4 1:4:5:8-tetramethylporphyrin-2:3:6:7-tetra-acetate, separable into fractions, red prisms (III), m.p. 255°, and needles, m.p. 197—206°. The spectrum of (IV) is intermediate between those of (I) and coproporphyrin IV Me_4 ester. When hydrolysed by alkali (IV) appears to

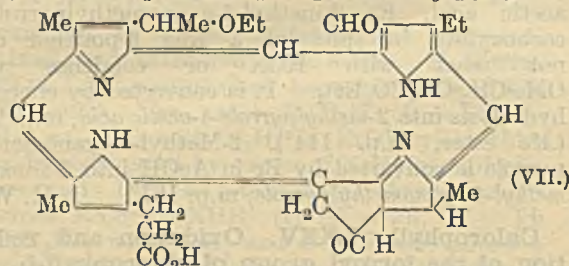
lose 2 CO_2H , giving the substance, $C_{30}H_{30}O_4N_4$, m.p. >350°. (IV) like (I) is decarboxylated by 1% HCl at 185° giving an octamethylporphyrin (V). (II) is transformed by boiling $HCO_2H-48\% HBr$ into 3:3':5:5'-tetramethylpyrrromethene-4:4'-diacetic acid hydrobromide, m.p. 246°, which is partly brominated and then condensed with 5:5'-dibromo-4:4'-dimethylpyrrromethene-3:3'-diacetic acid hydrobromide, darkens >208°, to a completely decarboxylated porphyrin the absorption spectrum of which is identical with that of (V). In general, therefore, CO_2H in tetramethylpyrrrintetra-acetic acids is less firmly united than in (I). (III) is oxidised by $K_2Cr_2O_7$ in 50% H_2SO_4 to methylcarboxymethylmaleimide, m.p. 159°; $\cdot CH_2 \cdot CO_2H$ is therefore stable in the maleimide nucleus and the analogous behaviour of carboxy-hæmatic acid supports the view that (I) is a porphyrin-acetic acid. Et 2-methyl-4-cyanomethylpyrrole-5-carboxylate in spite of a free β -position does not react with HCN or condense with $OMe \cdot CH_2 \cdot CH(CO_2Et)_2$. It is converted by energetic hydrolysis into 2-methylpyrrole-4-acetic acid, m.p. 210° (*Me* ester, m.p. 114°). 2-Methyl-4-cyanomethylpyrrole is converted by Br in $AcOH$ into 5-bromo-2-methyl-4-cyanomethylpyrrole, m.p. 167°. H. W.

Chlorophyll. LXXV. Oxidation and reduction of the formyl group of chlorophyll-b. H. FISCHER and W. LAUTENSCHLAGER (Annalen, 1936, 528, 9—39; cf. A., 1936, 1393).—Hydrogenation of chlorophyll-b derivatives in general resembles that of the α -compounds, but the CHO causes complications, reducing yields and necessitating careful choice of solvent. Under certain conditions the CHO is reduced to $CH_2 \cdot OH$ without reduction of the $CH:CH_2$. The CHO is oxidised to CO_2H by the oxo-reaction ($HI-O_2$) in HCl-AcOH without the $CH:CH_2$ being affected. Various reactions of the resulting acids are described. Hydrogenations given below are by H_2 -Pd-black. Phæophorbide-b (I) in dioxan gives (H_2) mesophæophorbide-b, sinters at about 225°, decomp. 242°, [α] 20 —185° in $COMe_2$. Rhodin-g, Me_3 ester in $COMe_2$ gives 30% and in dioxan 70% of mesorhodin-g, Me_3 ester, m.p. 214° [oxime, m.p. 234° (decomp.)]. Pyrophæophorbin-b (II) (a) in dioxan gives mesopyrophæophorbin-b, m.p. 256°, [α] 20 —324° in $COMe_2$, (b) in $COMe_2$ gives a mixture, and (c) best in $MeOH-H_2O-NH_3$ affords mesopyrophæophorbin-b-3-methanol (3-hydroxymethylmesopyrophæophorbide-a) (III), m.p. 219° (decomp.) [oxime, m.p. 244° (decomp.)]; Ac derivative, m.p. 193° (oxime, m.p. >315°). (I)



in $COMe_2-NH_3$ gives phæoporphyrin-b₆-3-methanol (3-hydroxymethylphæoporphyrin-a₅), m.p. 269° (de-

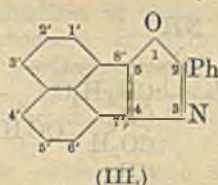
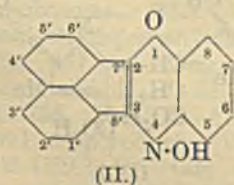
comp.) [*Ac* derivative, m.p. 277° (decomp.); *oxime*, sinters at 273°, m.p. >325°], converted by hot aq. Ba(OH)₂ into *rhodinporphyrin-g₇-3-methanol (3-hydroxymethylchloroporphyrin-e₆)* (IV), m.p. 258°. (II) gives similarly *phæoporphyrin-b₄-3-methanol (3-hydroxymethylphylloerythrin)*, m.p. 272° [*oxime*, m.p. 260° (decomp.)]. (I) and HI-O₂ in HCl-AcOH give *phæophorbide-b₇*, (*phæophorbide-a-3-carboxylic acid*) (V) [*Me₃* ester, sinters at about 260°, m.p. >330° [*oxime*, m.p. >345°; CHN₂·CO₂Me-additive compound, m.p. 253° (decomp.)]], isomerised by HCl-AcOH at 55–60° or by hydrogenation and re-oxidation to *phæoporphyrin-b₇* (*Me₃* ester, m.p. 275°) and hydrolysed by Ba(OH)₂ to *rhodin-g₈* (*chlorin-e₆-3-carboxylic acid*) (*Me₃* ester, m.p. 182°; gives by isomerisation *rhodinporphyrin-g₈* *Me₃* ester, m.p. 263°). (V) in hot C₅H₅N gives CO₂ and *pyrophæophorbide-b₅* (*pyrophæo-*



phorbide-a-3-carboxylic acid) (*Me₂* ester, m.p. 248°), also obtained from (II) by the oxo-reaction in HCl-AcOH and hydrogenated in AcOH to *phæoporphyrin-b₅* (*phylloerythrin-3-carboxylic acid*) (*Me₂* ester, m.p. 264°). (V) is decarboxylated in hot anhyd. HCO₂H, giving a 25% yield of *3-deformylpyrophæophorbide-b* (*3-demethylpyrophæophorbide-a*) (VI) and some of the *meso*-compound. The *Me* ester, m.p. 180° (*oxime*, *cryst.*; CHN₂·CO₂Me reaction positive), of (VI) with HI-AcOH or by hydrogenation and re-oxidation gives *3-deformylphæoporphyrin-b₄*, which gives the CH reaction with Br. (II) and HBr-AcOH at 41° give a product, which with MeOH gives 50% of *2-α-methoxyethylpyrophæophorbide-b* (VII), m.p. 255° (*oxime*, *cryst.*), but, if the temp. reaches 60°, *2-α-methoxyethylpyrophæoporphyrin-b₄*, m.p. 295° (decomp.), is obtained. The prep. of (II) from (I) by hot C₅H₅N is described.

R. S. C.

Acenaphthenequinone series. III. A. C. SIRCAR and D. C. CHOWDHURY (J. Indian Chem. Soc., 1936, 13, 709–715).—Acenaphthenequinone (I) and *o*-aminophenol condense in C₆H₆ to the *ψ*-base, *4-hydroxyacenaphthylene-7':8':2:3-1:4-benzoxazine* (II), m.p. 187° (cf. A., 1905, i, 930), decomposed by H₂SO₄, by SnCl₂-HCl, and by Br, giving (I), and converted by NHPh·NH₂ into a compound, m.p. 175°. (I) and 5-nitro-2-aminophenol yield the 7-NO₂-deriv-



ative of (II), which has two tautomeric forms, *aci*, orange, from EtOH, and *normal*, colourless, from

xylene, both m.p. 186° (decomp.), and which is decomposed as before, and is converted by NHPh·NH₂ into a compound, m.p. 161°. (I) and CH₂Ph·NH₂ with ZnCl₂ at 190° give *2-phenylacenaphthylene-7':8':4:5-oxazole* (III), m.p. 101°, with *2-phenyl-1-benzylacenaphthylene-7':8':4:5-glyoxaline*, m.p. 260°. Using NH₂Me, *2-methylacenaphthylene-7':8':4:5-oxazole*, m.p. 115–117°, and *2-methyl-1-ethylacenaphthylene-7':8':4:5-glyoxaline*, m.p. >290°, are formed. (I), CPhMe, Ac₂O, and H₂SO₄ give *4-acetoxy-5-phenylacenaphthylene-7':8':2:3-furan*, m.p. 257°. (I), NaOAc, and Ac₂O yield a compound (C₁₃H₅O₂)_n, m.p. >290° [converted by aq. KOH, followed by acid, into a compound, (C₅H₃O)_n, m.p. 240° (decomp.)], and a compound, (C₅H₃O)_n, converted by KOH and acid into *8-hydroxyacenaphthyl-7-glyoxylic acid lactone* (IV), m.p. 230–231°, also obtained from (I), CHO·CO₂H, and KOH-MeOH. (I) and KOH-EtOH give naphthalic anhydride and (IV).

E. W. W.

Synthetic compounds related to atophan.

P. K. BOSE and N. C. GUHA (J. Indian Chem. Soc., 1936, 13, 700–703).—Coumaranone, and its 6-, 5-, and 4-Me, and 5-OH derivatives, condenses with isatin in KOH-EtOH at 70° to *benzofuro-1':2':3:2-quinoline-4-carboxylic acid*, m.p. 277° (*Na* salt), and its 6'-, m.p. 286° [*Na* salt (+2H₂O)], 5'-, m.p. 281° (*Na* salt), and 4'-Me, m.p. 275°, and 5'-OH-derivative (I), m.p. 309°. Isatin also condenses with β-anisoylpropionic acid, and with α- and β-C₁₀H₇Ac, to 2-*p-anisyl*, m.p. 273°, and 2-*α*, m.p. 195–197°, and 2-β-naphthyl-quinoline-4-carboxylic acid, m.p. 248° (*Na* salt).

E. W. W.

3-Hydroxypyridine. II. Nitration and iodination, and 2:3-dihydroxypyridine. E. PLÁZEK and Z. RODEWALD (Rocz. Chem., 1936, 16, 502–508).—3-Hydroxypyridine (I) and HNO₃-H₂SO₄ at 30° yield 2-nitro-3-hydroxypyridine (II), m.p. 69–70° [*NH₄* salt, m.p. 146° (decomp.)], reduced by Na₂S₂O₄ in aq. NH₃ to 2-amino-3-hydroxypyridine (III), m.p. 164–168° (*picrate*, m.p. 225°). (I) and I in aq. KI afford an additive product, converted by NaOH into 2-iodo-3-hydroxypyridine, m.p. 193–195°, which with boiling aq. Ba(OH)₂ yields 2:3-dihydroxypyridine (IV), also obtained from (III) and HNO₂ at 0°. (III) and picryl chloride in EtOH-NaOH yield 7:9-dinitro-1-azaphenoxazine, m.p. 223°. (II) and (III) have been erroneously described as 6-nitro-(amino)-derivatives (F.P. 705,113), and (IV) as 2:5-dihydroxypyridine (Kudernatsch, A., 1898, i, 270).

R. T.

Condensation of furil and furoin. A. C. SIRCAR and S. C. GUHA (J. Indian Chem. Soc., 1936, 13, 704–708).—Furil, NH₃, and substituted benzaldehydes, at 165°, give 4'-, m.p. 235–236°, and 3'-hydroxy-, m.p. 265° (decomp.), and 4'-nitrophenyl-4:5-difurylglyoxaline, m.p. 175° (decomp.). With salicylaldehyde, *bis(furancarbo)-αβ-bis-(o-hydroxyphenyl)-ethylene-αβ-diamide*, no m.p. <307° (*Ac₂* derivative,

m.p. 246°), and with furfuraldehyde, *bis*(furan- α - β -difuryl- α - β -diamide, no m.p. <275°, are formed. Furoin, $\text{CH}_2\text{Ph}\cdot\text{CN}$, piperidine, and EtOH yield *phenylcyanoethylenedeoxyfuroin*; using hippuric acid, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, and CH_2Ac_2 , *benzamidocarboxy*-, *cyano*- and *acetyl-carbethoxy*-, *dicarbethoxy*-, and *diacetyl-ethylenedeoxyfuroin* are obtained; none melt <258°. With phloroglucinol, a compound, $\text{C}_{16}\text{H}_{10}\text{O}_6$, is formed. Furoin and $\text{CO}(\text{NH}_2)_2$ at 200° give *furildiurein*, $\text{CO}\langle\text{NH}\cdot\text{C}(\text{C}_4\text{H}_3\text{O})\cdot\text{NH}\rangle\text{CO}$; $\text{CS}(\text{NH}_2)_2$ gives *furildi-thiourein*. Furoin with $\text{CO}(\text{NH}_2)_2$ or $\text{CS}(\text{NH}_2)_2$ at 165° forms 4 : 5-difuryl-2-glyoxalone or -thioglyoxalone. With aromatic amines and their hydrochlorides, furoin yields 2 : 3-difuryl-indole, no m.p. <285°, -7-methyl-, m.p. 201—203°, and -5-methyl-indole, m.p. 210° (decomp.), and - α -, decomp. 240°, and - β -naphthindole, m.p. 184—185° (decomp.). E. W. W.

Manufacture of thiazole derivatives.—See B., 1937, 220.

Manufacture of thiazolium compounds.—See B., 1937, 220.

Manufacture of 4-alkyl-5-hydroxyalkylthiazoles.—See B., 1937, 121.

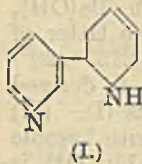
Organic fluorine [benzthiazole] compounds.—See B., 1937, 220.

Intermediates and dyes of anthraquinone series [benzthiazoles].—See B., 1937, 121.

Influence of the anion on the properties of thiocyanine dyes. A. I. KIPRIANOV and R. SCHUSSE (Proc. Charkov State Univ., 1936, 4, 49—53).—By condensing $\text{CMe}(\text{OEt})_3$ or $\text{CH}(\text{OEt})_3$ with the appropriate thiazole alkiodides etc. 8-methyl-2 : 2'-diethylthiocarbocyanine chloride, bromide, m.p. 245°, and iodide, 5 : 5' : 8-trimethyl-2 : 2'-diethylthiocarbocyanine bromide, m.p. 249°, and iodide, and 2 : 2'-diethyl-3 : 4 : 3' : 4'-dibenzthiocarbocyanine chloride, m.p. 189°, bromide, m.p. 281°, and iodide were prepared. The anion of the dye scarcely affects its sensitising properties. J. J. B.

Tobacco bases. XI. l-Anatabine, a new tobacco alkaloid. E. SPÄTH and F. KESZTLER (Ber., 1937, 70, [B], 239—243).—The isolation is described from a fraction of the subsidiary alkaloids of tobacco of l-anatabine, (I), $\text{C}_{10}\text{H}_{12}\text{N}_2$, b.p. 145—146° (corr.)/10 mm., $[\alpha]_D^{17} -177.8^\circ$ [6 : 6'-dinitro-2 : 2'-diphenate, m.p. 238—238.5° (vac.); monohydrochloride, $[\alpha]_D^{17} -61.9^\circ$ in H_2O ; dihydrochloride, $[\alpha]_D^{17} -65.4^\circ$ in H_2O ; dipicrate, m.p. 191—193° (vac.; decomp.); trinitro-m-tolylloxide, m.p. 191—192° (vac.; decomp.); picrolonate, m.p. 234—235° (vac.; decomp.)]. Dehydrogenation (Pd-sponge) of (I) under mild conditions affords 2 : 3'-dipyridyl whereas hydrogenation (Pd-sponge in AcOH) establishes the presence of 1 double linking and gives l-anabasine among other products. Treatment of (I) with Bz_2O in Et_2O gives a Bz derivative (II), b.p. 160—170° (bath)/0.01 mm., $[\alpha]_D^{18} -15.4^\circ$ in MeOH, thus, in conjunction with the optical activity of (I), establish-

ing the absence of the double linking from the neighbourhood of sec. N. Oxidation of (II) with KMnO_4 gives BzOH, nicotinic, and hippuric acid [which does not result from β -benzamidopropionic acid derivable from other possible structures for (I)]. (I) has therefore the constitution shown. It is probable that Ehrenstein's base (A., 1932, 177), incorrectly described as anabasine, and Pietet's nicotine are impure (I). H. W.



Derivatives of lupinine. M. KATZNELSON and M. KABUTSCHNIK (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 409—411).—With the object of synthesising lupinylbarbituric acid, chlorolupinane was treated with $\text{CHNa}(\text{CO}_2\text{Et})_2$, and gave *Et lupinylmalonate*, b.p. 199.5—200°/11 mm., which on hydrolysis gave *lupinylacetic acid* as a syrup, and with NaOEt and $\text{CO}(\text{NH}_2)_2$ gave a substance containing 14.44% Na. A. LI.

Furan analogue of cocaine. M. M. KATZNELSON and J. L. GOLDFARB (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 413—416).—*Furancocaine* (2-furoylecgonine Me ester), m.p. 142—143° [hydrochloride, m.p. 184.5°; platinichloride, m.p. 231° (decomp.); picrate, m.p. 167—169°], is produced in 66% yield from ecgonine Me ester and pyromucic anhydride (from pyromucic acid and Ac_2O in PhMe). Unlike thiophencocaine, it has not the anaesthetic properties of cocaine. A. LI.

Cinchona alkaloids in pneumonia. IV. Derivatives of ethylapocupreine [ethylapoquinine]. C. L. BUTLER, A. G. RENFREW, L. H. CRETCHER, and B. L. SOUTHER (J. Amer. Chem. Soc., 1937, 59, 227—229).—The K salt (I) of apocupreine, $[\alpha]_D -215^\circ$ (cf. A., 1935, 996), and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ in EtOH give some β -hydroxyethylapocupreine, amorphous, $[\alpha]_D -194^\circ$ in EtOH (dihydrochloride; Ac_2 derivative, $[\alpha]_D -51^\circ$ in EtOH). β - β' -Chloroethoxyethyl p-toluenesulphonate (from p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ at 142°) and (I) similarly give β - β' -chloroethoxyethylapocupreine (dihydrochloride, $[\alpha]_D -195^\circ$ in H_2O), which with EtOH-NaOEt at 96° (sealed tube) affords β - β' -ethoxyethoxyethylapocupreine (dihydrochloride, $[\alpha]_D -183^\circ$ in H_2O) and not the β -vinylxyethyl derivative. β -Butoxyethyl and β -phenoxyethyl, m.p. 75°, p-toluenesulphonates (prep.; loc. cit.) similarly lead to β -butoxyethyl- (dihydrochloride, $[\alpha]_D -198^\circ$ in H_2O) and β -phenoxyethyl-apocupreine, m.p. 178°, $[\alpha]_D -159^\circ$ in EtOH (dihydrochloride), respectively. Pharmacological data for some of the above compounds are compared with those for ethylapocupreine and optochin. H. B.

Aconitum alkaloids. III. Products of the degradation of aconite bases. E. F. ROGERS and W. FREUDENBERG (Ber., 1937, 70, [B], 349—354; cf. A., 1936, 618, 1277).—The structure of the hypothetical fundamental base $\text{C}_{19}\text{H}_{28}\text{NH}$ of the aconite alkaloids or, more simply, of the corresponding hydrocarbon $\text{C}_{20}\text{H}_{30}$ with avoidance of quaternary C atoms involves great angular anellation, all rings being doubly ortho-condensed, the presence of 2 5-membered and 4 6-membered rings, and the presence of 9 sec. C atoms.

The ring system appears new among alkaloids. Distillation of cryst. aconitine (I) with $\text{Ba}(\text{OH})_2$ gives basic and neutral products from the latter of which a substance (II), $\text{C}_{19}\text{H}_{24}\text{O}$, b.p. 215–220°/760 mm., is obtained in small yield; it is derived more copiously from technical, amorphous (I). (II) contains 1 active H and does not react with ketonic reagents or contain OMe. Hence probably OH is present and (II) then contains 5 rings. Determination of *C*-alkyl gives 3 mols. of AcOH corresponding with the presence of 3 Me. Catalytic micro-hydrogenation shows the presence of 3 double linkings which, according to the ultra-violet absorption spectrum, are not involved in a benzenoid arrangement. (II) is very readily autoxidised and is greatly decomposed by contact with mineral acid, Br, or I. It is hydrogenated (Pd-black in EtOH) to the compound (III), $\text{C}_{19}\text{H}_{28}\text{O}$, b.p. 192–194°/760 mm., or in presence of PtO_2 to the substance, (?) $\text{C}_{19}\text{H}_{30}\text{O}$, b.p. 180°/760 mm. (II) is very stable towards Se or Pd-C, by which it is converted into a product, $\text{C}_{19}\text{H}_{24}\text{O}$, b.p. 204°/760 mm., differing from (II) in being colourless. The residue obtained after removal of (II) contains a compound, (?) $\text{C}_{19}\text{H}_{24}\text{O}$, b.p. 240°/760 mm. Distillation of amorphous (I) with Zn dust affords the substances, $\text{C}_{16}\text{H}_{18}\text{O}_3$, b.p. 70–75°/0.2 mm., and $\text{C}_{18}\text{H}_{22}\text{O}$, b.p. 90°/0.2 mm., which closely resemble (II).

H. W.

Strychnos alkaloids. XCII. Isomerisation of the acid, $\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_2$, and oxidation of dihydrobrucine. H. LEUCHS and H. GRUNOW (Ber., 1937, 70, [B], 257–261).—Treatment of Hanssen's acid, $\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_2$, or its perchlorate with boiling NaOMe-MeOH affords an isomeride (perchlorate, $\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_2\cdot\text{HClO}_4$, $[\alpha]_D^{20} -46.2^\circ$ in H_2O) which absorbs 2 H when hydrogenated (PtO_2 in H_2O) and gives an Ac derivative (perchlorate, $[\alpha]_D^{20} -33.5^\circ$ in H_2O). It is oxidised by $\text{Ba}(\text{MnO}_4)_2$ at 0° ($\equiv 6^\circ$) to a substance (perchlorate, $\text{C}_{16}\text{H}_{20}\text{O}_6\text{N}_2\cdot\text{HClO}_4$, $[\alpha]_D^{20} +75.8^\circ$) or, in another experiment, to a compound [perchlorate, (?) $\text{C}_{16}\text{H}_{20}\text{O}_4\text{N}_2\cdot\text{HClO}_4$, $[\alpha]_D^{20} +80.4^\circ$, which does not show ketonic properties]. Oxidation of dihydrobrucine gives the compound, $\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_2$, and a substance (I), $\text{C}_{17}\text{H}_{22}\text{O}_5\text{N}_2$, m.p. $>300^\circ$, $[\alpha]_D^{20} -6.1^\circ$ in H_2O (perchlorate, $[\alpha]_D^{20} -12.5^\circ$ in H_2O ; semicarbazone perchlorate). (I) is also obtained by oxidation of the H_2 -acid, $\text{C}_{19}\text{H}_{24}\text{O}_6\text{N}_2$, with $\text{Ba}(\text{MnO}_4)_2$.

H. W.

Strychnine. III. Fission of strychnine and its derivatives with alkali. M. KOTAKE, K. MORI, and T. MITSUWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 31, 129–132).—Fusion of strychninolone with KOH gives a little BzOH and a 17% yield of β -indolyethylamine, smaller yields of which are obtained similarly from strychninonic acid (1%) and strychnine (3%). Leuchs' formula for strychnine thus is untenable.

J. W. B.

New aromatic arsenical compounds. I. Arsenical derivatives of diphenylmethane. E. V. ZAPPI and J. F. SALELLAS (Anal. Asoc. Quím. Argentina, 1936, 24, 65–72).— $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NH}_2\text{-}p)_2$ by Bart's method yields diphenylmethane-4:4'-diarsinic acid, decomp. about 250° [2:2'-(NO_2) $_2$ -

derivative (I), decomp. at high temp.], which with NaH_2PO_2 in dil. H_2SO_4 gives 4':4'''-arsenobisdiphenylmethane-4:4'-arsinic acid, does not melt, the 2:2':2'':2'''-(NO_2) $_4$ -derivative of which, decomp. at high temp., and 4:4':4'':4'''-diarsenobis-(2:2':2'':2'''-tetranitro)diphenylmethane, no m.p., are also prepared from (I) and NaH_2PO_2 . F. R. G.

Chloro-acid betaines. P. PFEIFFER and H. BÖTTCHER (Ber., 1937, 70, [B], 74–75; cf. A., 1935, 368).— $p\text{-NMe}_3\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_3\text{Cl}$ is converted by diazotisation and treatment with SbCl_3 into the stable salt, $p\text{-NMe}_3\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{SbCl}_4$, decomp. 139°, transformed by evaporation with HCl (d 1.075) into the betaine, $p\text{-NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{SbCl}_5$, the yield of which depends greatly on experimental conditions. The compound ($p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{SbCl}_5$) $\cdot\text{H}_5\text{C}_5\text{H}_5\text{N}$ (loc. cit.) is hydrolysed by aq. NH_3 to *p*-anisylstibinic acid.

H. W.

Selenophen. III. β -Nitroselenophen and orientation in the selenophen nucleus. S. UMEZAWA (Bull. Chem. Soc. Japan, 1937, 12, 4–8).—Selenophen-2-sulphonyl chloride with fuming HNO_3 at 0°—room temp. gives mainly its 4- NO_2 -derivative (I), m.p. 71–73.5°, and a little of an isomeride, probably the 5- NO_2 -compound, which could not be separated. Hydrolysis and steam-distillation of (I) from H_2SO_4 gives 4-nitroselenophen, m.p. 77–78.5°, (2:3:5- Br_3 -derivative, m.p. 100.5–102°), converted by fuming HNO_3 at $<0^\circ$ into the 2:4-(NO_2) $_2$ -derivative, m.p. 76–78° (also from the 2- NO_2 -compound) (adduct, m.p. 53–55°, with C_{10}H_8). J. W. B.

Structure of proteins. J. OVERHOFF (Chem. Weekblad, 1937, 34, 202–207).—A review. S. C.

Determination of carbon in slowly combustible materials of high carbon content, in a duplicated Würtz apparatus. A. G. BOGDANTSCHENKO (Zavod. Lab., 1936, 5, 498–499). R. T.

Exact determination of two organic compounds in presence of each other. I. MORGHEN (Ber., 1937, 70, [B], 195–200).—The method depends on measurement of the temp. at which a substance *A* in presence of varying amounts of a second substance *B* separates from a solvent when cooled (or warmed). The apparatus is figured. Results accurate to within $\pm 0.3\%$ are obtained with mixtures of 3-hydroxy-4-ethoxypropenylbenzene and isoeugenol. H. W.

Micro-determination of ammonia in presence of aliphatic amines.—See A., I, 197.

Separation of amino-acids. S. J. VON PRZYLECKI and K. KASPRZYK (Biochem. Z., 1937, 289, 243–250).—A method is described which depends on the fact that some NH_2 -acids are sol. in anhyd. fatty acids (basic NH_2 -acids), whilst some dissolve readily in fatty acids containing 0.2–5% of H_2O (neutral acids, asparagine, glutamine) and others are insol. in both of these media (aspartic, glutamic, and hydroxyglutamic acids, tyrosine, and cystine). Tables show the separation with various mixtures and the method is applied to a protein hydrolysate. P. W. C.

Colorimetric determination of free and combined cholesterol.—See A., III, 162.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

MAY, 1937.

New synthetic methods in organic chemistry. J. VAN ALPHEN (Chem. Weekblad, 1937, 34, 262—273).—A review. S. C.

Ebulliometric and tonometric researches on chemically pure liquids.—See A., I., 174.

Catalytic reactions among complex molecules.—See A., I, 252.

Catalytic isomerisation of *n*-octane. J. K. JURIEV and P. J. PAYLOV (J. Gen. Chem. Russ., 1937, 7, 97—99).—5—15% of *iso*-hydrocarbons are obtained by passing *n*-octane over various catalysts (Pt-C, Ni-Al₂O₃, Ni-ZnO, Al₂O₃, C) at 310°.

R. T.

cis-trans Rearrangement of ethylene compounds catalysed by molecular oxygen.—See A., I, 251.

Absorption of propylene and cyclopropane by solutions of sulphuric acid. F. F. RATMAN (J. Gen. Chem. Russ., 1937, 7, 14—17).—The rate of absorption by H₂SO₄ (*d* 1.59—1.83) of cyclopropane is > of propylene. The reactions take place in the surface film, between gas and H₂SO₄ mols., and involve rupture of the trimethylene ring.

R. T.

Separating butenes from butanes. Distillation of azeotropic mixtures with sulphur dioxide. M. P. MATUSZAK and F. E. FREY (Ind. Eng. Chem. [Anal.], 1937, 9, 111—115).—Separation of a mixture of C₄-hydrocarbons into a butane and a butene fraction is best accomplished by distilling the min.-boiling azeotropic mixtures formed with SO₂. V.p. and equilibrium concns. of liquid and vapour phases at different temp. are determined for samples of refinery gas fractions. The relationships between the SO₂ content of the liquid phase and the distribution of butenes and butanes between the vapour and liquid are linear. As the temp. of distillation increases, the molar concn. of SO₂ in the vapour phase increases linearly, the azeotropes decrease in hydrocarbon content, and the separation of the hydrocarbons is more difficult.

J. L. D.

Stereochemical studies. II. *cis*- Δ^2 -Butene from Δ^2 -butadiene. K. ZIEGLER, F. HÄFFNER, and H. GRIMM (Annalen, 1937, 528, 101—113; cf. A., 1934, 865).—Examination of the physical properties of the butene obtained by the successive action of alkali metal and amines on Δ^2 -butadiene shows it to be homogeneous and its behaviour when brominated and then treated with KOH-MeOH proves it identical with the Δ^2 -butene of higher b.p. obtained by Wislicenus from angelic acid. Reasons are advanced for regarding it as the *cis*-compound. Since *trans*- Δ^2 -butene is not isomerised

by contact with Li or Na or with their alkylanilides, the sterically homogeneous course of butadiene reduction is a peculiarity of the addition reaction in itself and is probably inherent to the initial stage of addition of metal. H. W.

Possible detection of conjugated carbon double linkings. K. MEINEL (Ber., 1937, 70, [B], 429—434).—The compounds obtained by treatment of a substance containing two conjugated ethylenic linkings or one ethylenic linking in conjugation with the C₆H₆ nucleus with 1 mol. of Br in EtOH give a red colour when mixed with a suspension of AgCNS in EtOH containing Fe⁺⁺⁺; products from substances which do not contain a conjugated system do not yield this colour or do so slowly and the final intensity is < that given by the former class. With CHPh:CH₂ the production of colour is not immediate and whilst that with CHPh:CH-CH₂OH or CHPh:CH-CHO is instantaneous, the max. intensity is observed only after several days. Substances with conjugated ethylenic linking (dihydrobenzene; dimethylbutadiene) give an immediate, pronounced colour. Substituents in the C₆H₆ nucleus may cause an immediate, marked colour (*isosaftrole*) or immediate max. intensity (*anethole*). The behaviour of crotonaldehyde depends on its age. PhBr does not react. The change is accelerated by AgBr, which causes the development of colour in cases in which it is not otherwise observed. The behaviour of raw and boiled linseed oil shows the presence of a conjugated system in the latter. The products of the reactions have not yet been isolated.

H. W.

Peroxide effect in the addition of reagents to unsaturated compounds. XIII. Addition of hydrogen bromide to butadiene. M. S. KHARASCH, E. T. MARGOLIS, and F. R. MAYO (J. Org. Chem., 1936, 1, 393—404).—In presence of antioxidants HBr and butadiene react rapidly (vac.; -78°) giving mainly α -bromo- Δ^2 -butene (I) and some α -bromo- Δ^3 -butene (II), the proportion of (I) formed decreasing with increasing temp. In presence of air or peroxides the main product is (II). At -12° (I) is converted into an equilibrium mixture [15% (I) and 85% (II)] by HBr in presence of a peroxide (*ascaridole*), but not by either of these reagents alone, except at higher temp. (30—45°), when HBr effects equilibration probably owing to the enhanced activity of minute quantities of peroxides at higher temp. Addition of HBr to (II) (which does not contain a terminal double linking) in presence either of antioxidants or of peroxides gives 80% of $\alpha\gamma$ - and 20% of $\beta\gamma$ -dibromobutane (III). A mixture of the same proportions is obtained from (I) and HBr in presence

of peroxides, but in presence of an antioxidant 60% of (III) is formed. These results are correlated with the effect of HBr and peroxides on the isomerisation of the bromobutenes. H. G. M.

Isomerisation of allene hydrocarbons by silicates. III. Isomerisation of tetramethylallene. IV. Tautomerism in the system allene-propylene. J. M. SLOBODIN (J. Gen. Chem. Russ., 1936, 6, 1806—1814, 1892—1896; cf. A., 1935, 957).—III. $\text{CMe}_2\text{Bu}^\beta\text{OH}$ is heated at 130—135° with $\text{H}_2\text{C}_2\text{O}_4$ to yield $\text{CMe}_2\text{CHPr}^\beta$, which with Br in Et_2O at -10° yields a mixture of $\text{CMe}_2\text{Bu}^\beta\text{Br}$ (I), $\text{CMe}_2\text{Br}\cdot\text{CHPr}^\beta\text{Br}$ (II), and $\text{CHBr}(\text{CMe}_2\text{Br})_2$ (III). (I) reacts further with Br at 60°, to yield (II), (III), $\text{CBr}_2(\text{CMe}_2\text{Br})_2$ (IV), and $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{CMeBr}\cdot\text{CH}_2\text{Br}$, and further yields of (III) may similarly be obtained from (II). (III) distilled from KOH at 135—140°/10 mm. yields $\beta\gamma$ -dibromo- $\beta\delta$ -dimethyl- Δ^2 -pentene, b.p. 96—97°/14 mm., from which $\text{CMe}_2\text{C}:\text{CMe}_2$ (V) is obtained by heating with Zn in 85% EtOH. (V) is also obtained from (IV) in the same way. Varying amounts of polymerides, and an equilibrium mixture of (V) (85%) and $\text{CMe}_2\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$ (VI) (15%), are obtained by passing (V), (VI), or (V) + (VI) vapour over floridin at 120—200°.

IV. A product containing polymerides and an equilibrium mixture of allene 38.5 and propylene 61.5% is obtained by passing allene vapour over floridin at 325°. R. T.

Hydrolysis of alkyl halides.—See A., I, 249.

Exchange reactions of iodine compounds.—See A., I, 259.

Iodo fluoromethane. A. E. VAN ARKEL and E. JANETZKY (Rec. trav. chim., 1937, 56, 167—168).—By the action of Hg_2F_2 on CH_2I_2 at about 120° iodo fluoromethane, b.p. 53.4°, has been obtained. R. C.

Synthesis of polychloro-compounds with aluminium chloride. III. Condensation of chloroethanes with chloroethylenes. H. J. PRINS (Rec. trav. chim., 1936, 56, 119—125).— $\text{CHCl}\cdot\text{CHCl}$ (I) readily adds HCl in presence of AlCl_3 giving $\text{CHCl}_2\cdot\text{CH}_2\text{Cl}$ (II), which reacts further with (I) giving two isomeric $\alpha\alpha\beta\gamma\delta$ -pentachlorobutanes, a solid (III), m.p. 48° (cf. A., 1932, 717), and a liquid (IV), b.p. 95.3—95.5°/11 mm. Both forms give α -chlorobutadiene, b.p. 68°, when treated with warm Zn—EtOH, and can be titrated in boiling EtOH with 0.1N-KOH, 1.44—1.59 mols. of HCl being evolved. (II), C_2HCl_3 , and AlCl_3 (40°; 7 days) give $\alpha\alpha\alpha\delta\delta$ -pentachloro- Δ^2 -butene, b.p. 78.5—80°/11 mm., which is stable to boiling 0.1% KMnO_4 , reduces AgNO_3 — NH_3 — H_2O in presence of a trace of alkali, and is also obtained from $\text{CCl}_3\cdot\text{CH}_2\text{Cl}$ and (I) in presence of AlCl_3 (40°, 10 days). (I), C_2HCl_3 , and AlCl_3 yield (III), (IV), and $\alpha\alpha\beta\beta\gamma\delta$ -heptachlorobutane, b.p. 97.5°/2 mm., reduced by Zn—EtOH to trichlorobutadiene. $\text{CHCl}_2\cdot\text{CHCl}_2$ (I), and AlCl_3 give a mixture from which only (III) could be isolated (cf. A., 1931, 597). C_2HCl_3 , C_2HCl_3 , and AlCl_3 give traces of a compound, m.p. 179—181°. H. G. M.

Photochemistry of some aliphatic nitroso-compounds. See A., I, 255.

Zinc oxides as catalysts in the methyl alcohol decomposition.—See A., I, 253.

Catalytic reduction of ethylene chlorohydrin. M. I. USCHAKOV and B. M. MICHAÏLOV (J. Gen. Chem. Russ., 1937, 7, 249—252).—Hydrogenation of $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ (I) in aq. NaOH in presence of Ni, Ni— SiO_2 , or Pd— CaCO_3 results in the production of EtOH (80—90%) and $(\text{CH}_2\cdot\text{OH})_2$ (II) (10—20%). The probable reactions are: (I) + NaOH \rightarrow $(\text{CH}_2)_2\text{O}$ (III) + H_2O + NaCl; (III) + $\text{H}_2 \rightarrow 2\text{EtOH}$; (II) + $\text{H}_2\text{O} \rightarrow$ (II). R. T.

Cobalt ethoxide and its hydrolysis. B. KANDELAKI and I. SETASCHVILI (Kolloid. Shurn., 1936, 2, 807—809; cf. A., 1935, 1349).—Co ethoxide, from CoCl_2 and NaOEt, affords with H_2O greenish-yellow sols of $\text{Co}(\text{OH})_2$, with EtOH + H_2O thixotropic gels. J. J. B.

Simultaneous dehydrogenation and dehydration of [amyl] alcohol by catalysts.—See A., I, 252.

Preparation of diacetylene glycols. J. S. SALKIND and M. A. AIZIKOVITSCH (J. Gen. Chem. Russ., 1937, 7, 227—233).—The reaction $2\text{OH}\cdot\text{CRR}'\cdot\text{CCH} \rightarrow (\text{OH}\cdot\text{CRR}'\cdot\text{C}\cdot\text{C})_2 + \text{H}_2$ takes place at room temp. in presence of CuCl , NH_4Cl , and O_2 , in the cases $\text{R} = \text{R}' = \text{Me}$, and $\text{OH}\cdot\text{CRR}' = 1$ -hydroxycyclohexyl. R. T.

Synthesis of glycerol. G. DARZENS (Compt. rend., 1937, 204, 506—507).—Diethoxyacetone (cf. A., 1934, 394) with H_2 —Ni (Raney) at room temp. affords β -hydroxy- $\alpha\gamma$ -diethoxypropane, which with conc. HCl under pressure at 120—125° gives glycerol in excellent yield. J. L. D.

Molecular compounds of dioxan. IV. Dioxanates of the halides of the alkali metals and of ammonium. H. RHEINBOLDT, A. LUYKEN, and H. SCHMITTMANN (J. pr. Chem., 1937, [ii], 148, 81—87; cf. A., 1933, 719).—The stable compounds, $\text{LiCl}\cdot\text{C}_4\text{H}_8\text{O}_2$, $\text{LiBr}\cdot\text{C}_4\text{H}_8\text{O}_2$, and $\text{LiI}\cdot\text{C}_4\text{H}_8\text{O}_2$, are obtained from their components directly or in EtOH. No compounds could be obtained from NaCl, NaBr, KCl, KBr, NH_4Cl , or NH_4Br , so that Li appears to resemble the elements of the second group of the periodic scheme in its behaviour. The compound $\text{NaI}\cdot 3\text{C}_4\text{H}_8\text{O}_2$ (I) is moderately stable whereas the substance $\text{KI}\cdot\text{C}_4\text{H}_8\text{O}_2$ speedily loses $\text{C}_4\text{H}_8\text{O}_2$ at room temp. The compound $\text{NH}_4\text{I}\cdot 2\text{C}_4\text{H}_8\text{O}_2$ resembles (I) in stability. H. W.

Polymembered ring systems. VII. Tendency of formation of rings containing oxygen. K. ZIEGLER and H. HOLL (Annalen, 1937, 528, 143—154).—A 10-membered ring containing 9 C and 1 O is much more readily obtained than one with 10 C and the formation of a 13-membered ring with 11 C and 2 O is less difficult than that of a ring with 13 C. $(\text{CH}_2\text{Br}\cdot\text{CH}_2)_2\text{O}$, from $(\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{O}$ and PBr_3 in $\text{C}_5\text{H}_5\text{N}$ or from technical $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$, is transformed by $\text{CHNa}(\text{CO}_2\text{Et})_2$ into the ester, $\text{O}[\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2]_2$, b.p. 175°/0.375 mm., hydrolysed to the tetracarboxylic acid, which passes into γ -hydroxybutyrolactone at 170°/vac. but is converted by piperidine at 100° into $\gamma\gamma'$ -dicarboxydipropyl

ether, b.p. 188°/0.45 mm. The corresponding *Me*₂ ester, b.p. 140—142°/14 mm., is reduced (Bouveault-Blanc) to *88'*-dihydroxydibutyl ether, b.p. 138°/0.6 mm., whence *88'*-dibromodibutyl ether, b.p. 142—147°/10 mm., and *88'*-dicyanodibutyl ether, b.p. 157°/0.4 mm. The nitrile is cyclised by NPhMeNa in Et₂O to 6-imido-5-cyanononamethylene oxide, m.p. 115—116°, in about 5% yield. Glycol di-*β*-bromoethyl ether, b.p. 140°/12 mm., and CHNa(CO₂Et)₂ afford the ester (CH₂)₂[O·CH₂·CH₂·CH(CO₂Et)₂]₂, b.p. 194—195°/0.375 mm., whence successively the corresponding tetracarboxylic acid, m.p. 131°, dicarboxylic acid, b.p. 222°/1.5 mm., m.p. 43—45°, and its *Me*₂ ester, b.p. 182°/10 mm. The latter substance is reduced to glycol di-*δ*-hydroxybutyl ether, b.p. 165—172°/0.5 mm., whence glycol di-*δ*-bromobutyl ether, b.p. 132—135°/0.5 mm., and glycol di-*δ*-cyanobutyl ether, b.p. 162°/0.01 mm. Cyclisation of the last compound followed by hydrolysis with acid leads to the keto-nitrile, $[\text{CH}_2]_2 \begin{smallmatrix} \text{O} \cdot [\text{CH}_2]_3 \cdot \text{CH} \cdot \text{CN} \\ \text{O} \cdot [\text{CH}_2]_4 \cdot \text{CO} \end{smallmatrix}$, b.p. 133°/0.01 mm., in 70% yield. H. W.

New synthesis of glycerides. V. P. GOLENDEEV (J. Gen. Chem. Russ., 1936, 6, 1841—1846).—Allyl esters with I in aq. EtOH yield *β*-iodomonoglycerides, which when heated with K salts of fatty acids at 100° give *αβ*-diglycerides; these yield triglycerides when heated at 100—120° in a H₂ atm. with a mixture of chloride and K salt of a fatty acid. R. T.

Electrolysis of salts in anhydrous glycerol.—See A., I, 254.

Reaction of dichromate with formate in light.—See A., I, 255.

Compounds of magnesium chloride with magnesium acetate and ethyl acetate.—See A., I, 256.

Reaction of magnesium *tert*-butyl chloride with ethyl acetate and propionate. K. I. KARASEV (J. Gen. Chem. Russ., 1937, 7, 179—184).—MgBu⁺Cl and EtOAc in Et₂O at 80—85° yield COMe₂, COMeBu⁺, CHMeBu⁺OAc, mesityl oxide, *βδ*-diketo-*εε*-dimethylhexane, b.p. 160—170° (Cu salt, m.p. 191.5°), and other unidentified products. EtCO₂Et under similar conditions yields chiefly ethyl-*tert*-butylcarbinyl propionate, b.p. 170—171°, together with *γ*-keto-*δ*-methyl-*ε*-ethyl-*Δ*⁸-heptene, b.p. 91—91.5°/18 mm. (phenylhydrazones, m.p. 128°). MgPr⁺Cl and PrCO₂Et at 0° afford CPr⁺₃·OH and CPr⁺₂. R. T.

Allylic transposition. VI. Allylidene diacetate. A. KIRRMANN (Bull. Soc. chim., 1937, [v], 4, 502—509; cf. A., 1936, 962).—CH₂:CH·CH(OAc)₂ (I), b.p. 76°/13 mm., and HCl give *γ*-acetoxyallyl chloride (II), b.p. 65°/12 mm., probably by direct replacement of OAc to give CH₂:CH·CHCl·OAc, followed by allylic rearrangement. The structure of (I) is proved by hydrogenation (Ni) to CHEt(OAc)₂; that of (II) is proved by the lability of the Cl (quant. hydrolysis by cold 0.1N-NaOH in <1 hr.), and reaction with (a) Br at -10° to give *β*-chloro-*α*-bromopropaldehyde, b.p. 62—63°/13 mm. (NaHSO₃-compound), and the diacetate, b.p. 119—122°/10 mm., (b) Br, followed by CrO₃, to give CH₂Cl·CHBr·CO₂H, m.p. 52°, and (c) HBr to give *γ*-chloro-*α*-bromopro-

pyl acetate, b.p. 95—96°/13 mm., oxidised to CH₂Cl·CH₂·CO₂H [and a little CH₂Br·CH₂·CO₂H, formed by reaction of (II) and HBr to give the acetoxybromide]. (II) and NaOAc in AcOH (not MeOH) re-form (I) (impure) by allylic rearrangement. Distillation of (II) at 760 mm. gives CH₂:CH·CHO and AcCl. EtCHO and AcCl give *α*-chloropropyl acetate, b.p. 36—37°/12 mm. (I) and HBr give similarly *γ*-acetoxyallyl bromide, b.p. 76—78°/12 mm. (dibromide, b.p. 105—107°/12 mm.). R. S. C.

Photochemical addition of hydrogen peroxide to the double linking. N. A. MILAS, P. F. KURZ, and W. P. ANSLOW, jun. (J. Amer. Chem. Soc., 1937, 59, 543—544).—Ethylenic compounds and 10% H₂O₂ in ultra-violet light give the corresponding glycols; free OH radicals are assumed to be first formed. Thus, crotonic acid gives dihydroxybutyric acid; maleic acid affords mesotartaric acid; Et maleate yields Et mesotartrate; allyl alcohol furnishes glycerol. H. B.

Spontaneous separation of stereoisomerides. C. NEUBERG (Biochimia, 1937, 2, 383—386; cf. A., 1906, i, 923).—The hexoic acid fraction (K salts) of a mixture of fatty acids obtained by bacterial putrefaction spontaneously separated, on keeping for 30 years, into the *d*- and *l*-forms. W. McC.

Electrolysis of *Δ*^γ- and *Δ*^β-hexenoic acid. F. FICHTER and T. HOLBRO (Helv. Chim. Acta, 1937, 20, 333—345).—Present experience and that of other workers shows that the interposition of <2 CH₂ between CO₂H and the double linking is generally necessary for the success of Kolbe's hydrocarbon synthesis from unsaturated acids. Apart from other considerations, its failure with aromatic acids containing CO₂H directly united to the C₆H₅ nucleus is therefore readily followed. The reason is not obvious since BzOH and various unsaturated acids give peroxides which readily decompose thermally in the sense of Kolbe's synthesis. Electrolysis of a solution of *Δ*^γ-hexenoic acid and K *Δ*^γ-hexenoate at Pt electrodes gives *Δ*^γ-pentadiene and a neutral oil containing *Δ*^γ-penten-*α*-ol (identified as the phenylcarbamate, C₁₂H₁₅O₂N, b.p. 136—142°/0.15 mm.), small amounts of *Δ*^β-decadiene, b.p. 168—170°/735 mm. (oxidised to adipic acid and transformed by Br in CS₂ into *βγθ*-tetrabromodecane, b.p. 140—150°/0.1 mm.), and *Δ*^γ-pentenyl *Δ*^γ-hexenoate. *Δ*^β-Hexenoic acid affords *Δ*^{αβ}-pentadiene and *Δ*^β-pentenyl *Δ*^β-hexenoate but not *Δ*^γ-decadiene. H. W.

Autoxidation of linoleic and linolenic acid in buffered solution in presence of porphyrins. K. HINSBERG and R. AMMON (Z. physiol. Chem., 1937, 246, 139—148).—The process is restricted by addition of haemin and still more by that of haemato-, copro-, or isouro-porphyrin. No restriction is produced by non-fluorescent esters of porphyrins or by porphyrins in which fluorescent power has been destroyed by irradiation with ultra-violet light. W. McC.

Electrochemical oxidation of copper lactate. W. E. BRADT and H. O. FALLSCHER (Trans. Electrochem. Soc., 1937, 71, Preprint 15, 157—169).—Cu lactate (I) is oxidised at >60° by aq. Cu(NO₃)₂

without the passage of a current, the products being CuC_2O_4 , basic Cu nitrate, CO, CO_2 , and AcOH. Cu pyruvate is not formed (cf. Smull and Subkow, A., 1923, i, 298). Electrochemical oxidation of (I) at $<60^\circ$ with a high $[\text{Cu}(\text{NO}_3)_2]$ yields CO_2 , AcOH, and MeCHO. Above 60° the ordinary thermal oxidation is superposed, CO_2 and CuC_2O_4 being the chief products. The insol. ppt. is CuC_2O_4 containing basic Cu nitrate. 67% of the (I) oxidised by $\text{Cu}(\text{NO}_3)_2$ forms equimol. amounts of $\text{H}_2\text{C}_2\text{O}_4$ and CO_2 .

H. J. E.

Isomerism of chloralides. I. N. M. SHAH and R. L. ALIMCHANDANI (J. Univ. Bombay, 1936, 5, Part II, 132—136).—*cis-trans*-Isomerism of chloralides is regarded as demonstrated by isolation of two forms of the chloralides of the following acids: lactic, (I) b.p. $210\text{--}212^\circ$, (II) m.p. $56\text{--}57^\circ$ [(I) gives (II) when kept or distilled]; *r*-tartaric, m.p. 161° and $213\text{--}215^\circ$; mucic, m.p. 198° and 174° , the latter being obtained by crystallisation from EtOH. Each pair of forms gives the same reduction product with Zn-AcOH.

R. S. C.

Acetone compounds of dihydroxy-acids. I. Acetone of *o*-dihydrostearic acid. V. I. ESAROV (J. Gen. Chem. Russ., 1936, 6, 1818—1822).—*cis-o*-Dihydroxystearic acid (m.p. 95°), COMe_2 , and HCl (at room temp.; 6 days) give *o*-isopropylidenedioxystearic acid (I), an oil, in 85% yield. Under analogous conditions the *trans*-acid, m.p. 132° , gives 12—16% yields of (I), pointing to partial conversion of the *trans*- to the *cis*-form under the conditions of the experiment.

R. T.

Production of oxidoethylene- $\alpha\beta$ -dicarboxylic acid by a mould.—See A., III, 182.

Detection of malic acid by means of brucine. C. J. VAN NIEUWENBURG and L. M. BROBBEL (Mikrochem., Molisch Festschr., 1936, 338—341).—*L*-Malic acid (I) forms with excess of brucine a salt of characteristic cryst. habit. Less characteristic salts are formed by other org. acids. Mineral acids interfere, but (I), in 0.3% concn., may be detected in presence of a large excess of lactic acid or sugars.

J. S. A.

Condensation of diacetyltartaric anhydride with aromatic amines. R. MAŁACHOWSKI (Rocz. Chem., 1937, 17, 33—35).—The compound described by Wróbel (A., 1934, 309) as *N*-phenyl-2:3-dihydrooxazine-2:3-dicarboxylphenylimide is actually the dianilide of tartaric acid, and those described as 3:3'-diketo-5:5'-dimethyldihydro-2:2'-di-indolyl and 3:3'-diketo-1:1':2:2':3:3':4:4'-tetrahydro-2:2'-diquinolyl (this vol., 77) are in reality the di-*p*-toluidide of tartaric acid and *o*-toluidino-*N*-*o*-tolyl-maleimide, respectively. The structure of the Br- and NO_2 -derivatives of the above compounds should be revised accordingly.

R. T.

Physiological degradation of citric acid.—See A., III, 174.

Nature and properties of the dienolic group of vitamin-C. N. A. BEZSSONOFF (Biochimia, 1937, 2, 230—241).—The colours produced by the interaction of vitamin-C, quinol (I), and pyrogallol and phosphomolybdic acid (II) and the fact that no colour

is produced when (II) is mixed with pyrocatechol show that the dienolic groups of -C and (I) are polar.

W. McC.

Synthesis of ascorbic acid. B. HELFERICH and O. PETERS (Ber., 1937, 70, [B], 465—468).—Condensation of glucose with $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (I) in presence of NaCN in absence of air affords *glucoheptascorbic acid* which crystallises with difficulty. The synthesis can be extended to all aldoses and to their acetates which become hydrolysed during the change. Acetylated cyanohydrins are particularly suitable. Thus *d*-threose cyanohydrin tetra-acetate and (I) give *d*-xyloascorbic acid in very good yield.

H. W.

Synthesis of vitamin-C from sucrose. P. P. T. SAH (Ber., 1937, 70, [B], 498—499).—Sucrose (I) is hydrolysed by acid to *d*-glucose (II) and *d*-fructose (III), which are reduced by Na-Hg to *l*-sorbitol and *d*-mannitol. Oxidation with $\text{Br}\cdot\text{H}_2\text{O}$ yields a mixture of (II), (III), *l*-gulose, and *l*-sorbosose the last two of which remain after fermentation with yeast. They afford *l*-gulosazone, converted by PhCHO into *l*-gulosone, which is oxidised to *l*-ketogulonic acid (IV). Esterification of (IV) by $\text{CH}(\text{OMe})_3$ in presence of HCl-MeOH followed by enolisation of the Me ester by NaOMe and neutralisation of the product with HCl-EtOH gives *l*-ascorbic acid. (I) can be replaced advantageously by (II) or carbohydrates which yield (II). Galactose can also be used.

H. W.

Ferrous gluconate, $[\alpha]_D +3.5^\circ$ in H_2O .—See A., III, 171.

Stereoisomeric forms of methylenedi- α -thiopropionic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1937, 12, A, No. 15, 12 pp.).—Saturation of $\text{SH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ in 40% CH_2O with HCl ppts. a mixture of the cryst. *dl*-form (I), m.p. $155\text{--}156^\circ$, and an oil from which the *meso*-form, m.p. $81.5\text{--}82.5^\circ$ (quinine salt + $2\text{H}_2\text{O}$), of methylenedi- α -thiopropionic acid is isolated. Fractional crystallisation of the quinine salt of (I) from 45% COMe_2 affords (—), m.p. $82.5\text{--}83.5^\circ$, $[\alpha]_D^{25} -376.3^\circ$ in 0.5*N*-HCl (quinine salt + $4\text{H}_2\text{O}$), and (from the mother-liquor) (+)-methylenedi- α -thiopropionic acid, m.p. $82.5\text{--}83.5^\circ$, $[\alpha]_D^{25} +375.2^\circ$ in 0.5*N*-HCl (quinine salt + H_2O). A mixed m.p. diagram shows the existence of a 1:1 mol. compound, m.p. 80.7° , of the (—) and *meso*-forms. The primary *K* for both *meso*- and *dl*-forms (by conductivity measurements) is 4.2×10^{-4} .

J. W. B.

Catalysis of formaldehyde condensation by hexoses. IV. Vitamin-C as catalyst for synthesis of carbon chains. A. M. KUZIN (Biochimia, 1937, 2, 127—134; cf. A., 1936, 703).—In presence of $\text{Ca}(\text{OH})_2$ at 37° CH_2O yields no sugar in <5 hr. but is completely converted into sugar in 2 hr. when ascorbic acid is added. *iso*Ascorbic acid (I) is less effective because of dissociation, with production of catalytically inactive ions, of the Ca enolate but the Me ether of (I) is a powerful catalyst, the methylation causing a 40—50% increase in the activity. In neutral and acid media CH_2O combines with (I).

W. McC.

Decomposition of acetaldehyde catalysed by bromine. W. BRENSCHEDE and H. J. SCHUMACHER (Ber., 1937, 70, [B], 452—456).—The decomp. of

MeCHO at 300–400° in presence of Br is not due to catalytic action of the latter. The substances react very rapidly with production mainly of HBr and MeBr, which with a less-volatile, unidentified Br-compound accelerate the reaction to the expected extent. Br is not regenerated in the change.

H. W.

Aldol condensation of *n*-butaldehyde. V. S. BATALIN and S. E. SLAVINA (J. Gen. Chem. Russ., 1937, 7, 202–206).—Pr^aCHO in Et₂O and 10% NaOH at 25–40° yield *n*-butyraldol (8-hydroxy-γ-aldehydoheptane), b.p. 92–94°/5 mm. (oxime, b.p. 148–149°/613 mm.). At 40–50° the sole product of the reaction is γ-aldehydo-Δ⁸-heptene (oxime, b.p. 99–101°/8 mm.).

R. T.

Production of dihydroxyacetone by the action of *Acetobacter suboxydans* on glycerol.—See A., III, 182.

Artemisia ketone. Y. ASAHINA and S. TAKAGI (Helv. Chim. Acta, 1937, 20, 220–221).—Oxidation of artemisia ketone (I) by KMnO₄ gives CMe₂(CO₂H)₂ whilst its H₄-derivative and CrO₃ give CMe₂Et·CO₂H, thereby establishing the structure of one part of the mol. Hydroxylaminoisartermisia ketone, CH₂:CH·CMe₂·CO·CH₂·CMe₂·NH·OH, is converted by HgO into the corresponding NO-derivative, which is colourless when solid but blue when molten or dissolved; hence NO replaces a *tert.* H. Artemisia oil contains (I) and isoartermisia ketone (II) since it gives a mixture of products when treated with NH₂·CO·NH·NH₂ in cold solution. Prolonged action of acids isomerises (I) to (II). Semicarbazoinisartermisia ketone (III) is transformed by HNO₂ into the corresponding, sparingly sol. azide, m.p. 156°, which can be used for the determination of (III). Hydroxylaminoisartermisia ketone, m.p. 170°, is oxidised by HgO in boiling CHCl₃ to nitrosodihydroartermisia ketone, m.p. 64°. The constitutions, CH₂:CH·CMe₂·CO·CH₂·CMe₂·CH₂ and CH₂:CH·CMe₂·CO·CH·CMe₂, are ascribed to (I) and (II), respectively.

H. W.

[Artemisia ketone.] L. RUZICKA (Helv. Chim. Acta, 1937, 20, 221).—In reply to Asahina (preceding abstract), it is pointed out that the colour reactions of a NO-derivative can scarcely be regarded as conclusive evidence of the C skeleton of a compound particularly as it has not been found possible to oxidise the terminal CMe₂ to COMe₂.

H. W.

Gravimetric micro-determination of acetoin and diacetyl. R. KUNZE (Mikrochem., Molisch Festschr., 1936, 279–289).—Acetoin is oxidised to Ac₂ by warming with FeCl₃ at 50–60°. The total Ac₂ is finally distilled at 90° into a solution of NH₂OH·HCl + NaOAc + NiCl₂, kept at 50°. The pptd. Ni dimethylglyoxime is collected and weighed, preferably by the Donau technique.

J. S. A.

Hydrogenation of isobutyroin under the conditions of alcoholic fermentation. A. E. FAVORSKI and (MLLE.) F. J. RUDNEVA (Bull. Soc. chim., 1937, [v], 4, 435–438).—Addition of COPr^a·CHPr^a·OH (I) to yeast and aq. sucrose gives a little Pr^aCO₂H, β-dimethylhexane-γδ-diol (II), m.p. 72–74°, b.p. 93–97°/12 mm., and Pr^aCHO. Probably (I) gives

2 mols. of Pr^aCHO, the (II) and acid being formed by reduction of (I) by Pr^aCHO.

R. S. C.

Keto-ethers. II. Alkyl α-α'-γ'-dichloroisopropoxyethyl ketones. B. B. ALLEN [with H. R. HENZE] (J. Amer. Chem. Soc., 1937, 59, 540–542; cf. A., 1934, 871).—α-Chloroethyl αγ-dichloroisopropyl ether, b.p. 89–90°/18 mm. (from αγ-dichlorohydrin, paracetaldehyde, and dry HCl), and CuCN in C₆H₆ give α-α'-γ'-dichloroisopropoxypropionitrile (I), b.p. 99°/4 mm., which with the requisite Grignard reagent affords Me, b.p. 105–106°/5 mm. (using MgMeBr) (semicarbazone, m.p. 110·5°), Et, b.p. 117°/7–7·5 mm. (semicarbazone, m.p. 131·5–132°), Pr^a, b.p. 127·5°/5 mm. (semicarbazone, m.p. 114·5°), Pr^a, b.p. 124–125·5°/12 mm., Bu^a, b.p. 136–136·5°/6 mm. (semicarbazone, m.p. 94·8°), Bu^β, b.p. 127–128°/5–6 mm., sec-Bu, b.p. 129–130°/5 mm., n-amyl, b.p. 148·5–149°/5–5·5 mm. (semicarbazone, m.p. 108·6°), and isoamyl, b.p. 143–144°/5 mm. (semicarbazone, m.p. 111·5°), α-α'-γ'-dichloroisopropoxyethyl ketones. (I) and MgMeI give some Me α-α'-chloro-γ'-iodoisopropoxyethyl ketone [semicarbazone, m.p. 123–124° (decomp.)]. Howells and Little's modification (A., 1932, 854) of the Hoesch test is valueless as a micro-method for the identification of chloroalkoxy-nitriles; (I) and s-C₆H₃(OH)₃ thus afford a little of a trihydroxyphenyl α-α'-γ'-dichloroisopropoxyethyl ketone, m.p. 175·5°. All b.p. and m.p. are corr.

H. B.

Reaction of sugars with boric acid.—See A., I, 249.

First identifiable products of the anaerobic catalytic decomposition of sugars. A. N. BACH, E. P. ALEXEEVA, and V. P. DREVING (Biochimia, 1936, 1, 75–93).—Glucose in 0·1–0·5*N*-NaOH, in absence of O₂, and presence of Pt-black gives equal amounts of gluconic acid (I), sorbitol (II), and H₂. Similarly, galactose yields galactonic acid and dulcitol, arabinose gives arabonic acid (III) and arabitol, and mannose affords mannonic acid and mannitol. Fructose affords HCO₂H, MeOH, (I), (II), and (III); the production of (I) and (II) is ascribed to conversion of fructose into glucose in the alkaline medium.

R. T.

Active form of simple sugars. II. Comparative study of oxidation of glucose 6-phosphate and glucose. A. KUZIN and A. KOTSCHKIN (Biochimia, 1936, 1, 676–684).—The velocity of oxidation by Br of glucose-6-phosphoric acid in acid solution >, and in neutral solution <, that of glucose.

R. T.

Bromine oxidation and mutarotation measurements of the α- and β-aldoes. H. S. ISBELL and W. W. PIGMAN (J. Res. Nat. Bur. Stand., 1937, 18, 141–194).—Vals. of the rate of oxidation by Br-H₂O, [α], and the rates and heats of activation of mutarotation are recorded for α-d- and β-d-glucose, α-d- and β-d-galactose, α-d-talose, α-d- and β-d-mannose, mannose-CaCl₂·4H₂O, α-d-gulose-CaCl₂·H₂O, α-d-xylose, α-d- and β-d-lyxose, α-l-arabinose, β-l-arabinose-CaCl₂·4H₂O, d- and l-ribose, α-l-rhamnose, α- and β-lactose, and β-maltose. The results are discussed in relation to the structure of the sugars, particularly

their classification into α - and β -isomerides, and to the composition of the equilibrium sugar solutions.

A. J. E. W.

Catalytic oxidation of carbohydrates and related compounds by oxygen in the presence of iron pyrophosphates. IV. Methyl alcohol, formaldehyde, formic acid, sodium formate, ethyl alcohol, acetaldehyde, acetic acid, sodium acetate, glycol, glycollic acid, sodium glycolate, oxalic acid, and sodium oxalate. E. F. DEGERING (Proc. Indiana Acad. Sci., 1934, 44, 129—131).—With the exception of MeCHO the above do not give CO₂ on oxidation and could thus be detected as end products in sugar oxidation.

CH. ABS. (r)

Sulphuric esters of sugars. I. Rough estimate of proportion of glucose polysulphates in their mixture. T. SODA and W. NAGAI (J. Chem. Soc. Japan, 1935, 56, 1258—1262).—Such an estimate may be made from the hydrolysis velocity coeff.

CH. ABS. (r)

Action of sulphuric acid on glucose and sucrose. K. A. N. RAO and P. L. N. RAO (J. Annamalai Univ., 1937, 6, 155).—Glucose undergoes no charring with conc. H₂SO₄ below 25° or with dil. (1:1) acid at 50—80°. Sucrose darkens rapidly in both cases.

F. L. U.

Preparation and properties of 2:3:4:6-tetraethyl- α -methyl-*D*-glucoside and of 2:3:4:6-tetraethyl-*D*-glucose. A. R. PADGETT and E. F. DEGERING (J. Org. Chem., 1936, 1, 336—339).—Details for the prep. of 2:3:4:6-tetraethyl- α -methyl-*D*-glucoside (I), b.p. 94—96°/0.15 mm. and 97—100°/0.2 mm., $[\alpha]_D^{20} + 76.5^\circ$ in EtOH, from α -methyl-*D*-glucoside (II) by modifications of the known methods for methylation are recorded. (I) was purified by fractionation with a Podbielniak column, and is hydrolysed to 2:3:4:6-tetraethyl-*D*-glucose, m.p. 80—82°. It is assumed that the pyranoid ring structure of (II) is stable to ethylation.

H. G. M.

Structure of agar-agar. E. G. V. PERCIVAL, J. MUNRO, and J. C. SOMERVILLE (Nature, 1937, 139, 512—513).—Simultaneous deacetylation and methylation of acetylated agar gives an apparently homogeneous, fully methylated agar (OMe 31%), $[\alpha]_D^{15} - 78^\circ$ in CHCl₃, hydrolysed to an acid, and a mixture of methylated sugars (approx. 75%) which on conversion into the glycosides gave cryst. trimethyl- α -methylgalactoside. The trimethylgalactose is probably the 2:4:6 compound. The main carbohydrate portion of agar-agar probably consists of β -galactopyranose units linked at positions 1 and 3.

L. S. T.

D- β -Galaheptose and its derivatives. R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 548—551).—Details are given for the isolation of *D*- β -galaheptonic acid (I) (as phenylhydrazide, m.p. 189—190°) from the reaction product from *D*-galactose and HCN (A., 1936, 193). The lactone of (I) with liquid NH₃ affords *D*- β -galaheptonamide, m.p. 170—171°, $[\alpha]_D^{20} - 20^\circ$ in H₂O; reduction (Na—Hg, H₂O) gives α -*D*- β -galaheptose (II), m.p. 196—197° (decomp.), $[\alpha]_D^{20}$ (in H₂O) about $-19^\circ \rightarrow -53.95^\circ$, which closely resembles the configuratively related *L*-glucose in chemical and physical properties. Acetylation (Ac₂O,

NaOAc) of (II) affords α -*D*- β -galaheptose hexa-acetate (III), m.p. 151—152°, $[\alpha]_D^{20} + 30.2^\circ$ in CHCl₃, rearranged by cold Ac₂O—AcOH—conc. H₂SO₄ into β -*D*- β -galaheptose hexa-acetate, m.p. 100—101°, $[\alpha]_D^{20} - 55.8^\circ$ in CHCl₃. The syrup from (III) and AcOH—HBr with MeOH + Ag₂CO₃ gives α -methyl-*D*- β -galaheptoside penta-acetate, m.p. 122—123°, $[\alpha]_D^{20} + 51.8^\circ$ in CHCl₃, converted by MeOH—NH₃ into α -methyl-*D*- β -galaheptoside, m.p. 182—183°, $[\alpha]_D^{20} + 36^\circ$ in H₂O. (II) and CH₂Ph—SH in conc. HCl afford *D*- β -galaheptose dibenzyl mercaptal, m.p. 146—147°, $[\alpha]_D^{20} + 73.8^\circ$ in C₆H₅N (hexa-acetate, m.p. 82—83°, $[\alpha]_D^{20} + 9.2^\circ$ in CHCl₃). All m.p. are corr.

H. B.

New reagents for recognising ketoses. E. VOTOČEK and R. MULLER (Coll. Czech. Chem. Comm., 1937, 9, 120—125).—The sugar is treated, at 100°, with Ac₂O saturated with HCl (or with Ac₂O—AcCl), and with $\alpha\alpha'$ -dinaphthylamine, or with 1:2:7:8-dibenzocarbazole (I), which give stable, intense violet colorations with ketoses but not with aldoses. 3:4:5:6-Dibenzocarbazole similarly gives (less intense) green colorations with ketoses. With hydroxymethylfurfuraldehyde (II), (I) gives a violet colour, changing to blue; the colour produced by ketoses is thus not necessarily due to (II), but possibly to chloromethylfurfuraldehyde. The colour reactions of the last, and of furfuraldehyde, are examined.

E. W. W.

Rotatory power of alkaline solutions of sucrose.—See A., I, 236.

Polysaccharides synthesised by micro-organisms. III. Molecular structure of galactocarlose produced from glucose by *Penicillium Charlesii* (G. Smith). W. N. HAWORTH, H. RAISTRICK, and M. STACEY (Biochem. J., 1937, 31, 640—644).—Galactocarlose (I) is hydrolysed by 0.01*N*-HCl at 100°, giving a 90% yield of *D*-galactose. Methylgalactocarlose is hydrolysed by boiling 3% MeOH—HCl, yielding 2:3:5:6-tetramethyl-methylgalactofuranoside, $[\alpha]_{D780}^{20} - 67.0^\circ$, and 2:3:6-trimethyl-methylgalactoside, which can be characterised by oxidation to the respective lactones. (I) has a min. chain length of 9—10 units of β -galactofuranose linked through the 1:5 positions.

P. G. M.

Hydrogenation of glucosides in presence of active nickel. M. M. JANOT and T. TOMESCO (Compt. rend., 1937, 204, 504—506).—Salicin, arbutin, aesculin, and phloridzin are not reduced with H₂—Ni (Raney) at 9—12° in aq. EtOH—NaOH (cf. A., 1934, 992); other glucosides are reduced, whilst vanillin, aucubin, and amygdalin are hydrolysed after reduction.

J. L. D.

Gluconointol, m.p. 196—198°, $[\alpha]_D^{20} + 1.5^\circ$ in H₂O (Ac derivative, m.p. 179—180°). Glucosides, (?) C₂₀H₂₄O₁₁, m.p. 154—155°, $[\alpha]_D^{20} - 92.6^\circ$ in EtOH, and (?) C₁₃H₂₀O₉, m.p. 172—174°, $[\alpha]_D^{20} - 163.6^\circ$ in H₂O.—See A., III, 190.

Emulsin. XXVIII. *p*-Toluenesulphonic esters of vanillin- β -*D*-glucoside and their fission by emulsin of sweet almonds. B. HELFERICH and S. GRÜNLER (J. pr. Chem., 1937, [ii], 148, 107—116).—Hydrolysis of the susceptible vanillin- β -*D*-glucoside by emulsin is inhibited by the entry of a single

p -C₆H₄Me·SO₂ in any part of the mol. β -D-Glucose 1 : 2 : 3 : 4-tetra-acetate 6- p -toluenesulphonate is converted by HBr-AcOH into 1-bromo-D-glucose 2 : 3 : 4-triacetate 6- p -toluenesulphonate, m.p. 89—90°, $[\alpha]_D^{20} +165^\circ$ in CHCl₃, converted by vanillin and KOH in H₂O-COMe₂ at room temp. into vanillin- β -D-glucoside 2 : 3 : 4-triacetate 6- p -toluenesulphonate, m.p. 161—162°, $[\alpha]_D^{19} -60.5^\circ$ in CHCl₃, deacetylated by NaOMe in boiling MeOH to vanillin- β -D-glucoside 6- p -toluenesulphonate, m.p. (indef.) 125—130° after softening at about 85° or (+3H₂O) m.p. about 80°, (anhyd.) $[\alpha]_D^{21} -92^\circ$ in CHCl₃. Similarly, 1-bromo-D-glucose 2 : 3 : 6-triacetate 4- p -toluenesulphonate is converted into vanillin- β -D-glucoside 2 : 3 : 6-triacetate 4- p -toluenesulphonate, m.p. 168—170° (decomp.) in bath preheated to 150°, $[\alpha]_D^{19} -49^\circ$ in CHCl₃, hydrolysed by NaOMe in MeOH-CHCl₃ at -20° to vanillin- β -D-glucoside 4- p -toluenesulphonate, (+2H₂O), m.p. 162—165° after softening at about 150° (+0.5H₂O), and (anhyd.), m.p. 165—170° $[\alpha]_D^{20} -53^\circ$ in C₅H₅N. 1-Bromo-D-glucose 2 : 4 : 6-triacetate 3- p -toluenesulphonate affords vanillin- β -D-glucoside 2 : 4 : 6-triacetate 3- p -toluenesulphonate, m.p. 170—171°, $[\alpha]_D^{19} -16^\circ$ in CHCl₃, whence vanillin- β -D-glucoside 3- p -toluenesulphonate (+3H₂O) and (anhyd.), m.p. 126—128° after softening at 90°, $[\alpha]_D^{21} -25^\circ$ in CHCl₃. 1-Chloro- is converted by HBr in AcOH containing a little Ac₂O at room temp. into 1-bromo-D-glucose 3 : 4 : 6-triacetate 2- p -toluenesulphonate, m.p. 113—115°, $[\alpha]_D^{18} +176^\circ$ in CHCl₃, which, under strictly defined conditions, is converted into vanillin- β -D-glucoside 3 : 4 : 6-triacetate 2- p -toluenesulphonate, m.p. 132—133°, $[\alpha]_D^{18} -50.5^\circ$ in CHCl₃, and thence into vanillin- β -D-glucoside 2- p -toluenesulphonate (+1H₂O), m.p. (anhyd.) 165—168° after slight softening, $[\alpha]_D^{20} -127^\circ$ in C₅H₅N. H. W.

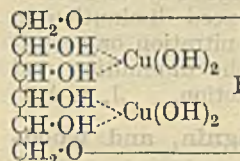
Glucoside of the flavone of the white flower.
IV. Constituents of *Cosmos bipinnatus*, Cav.
 T. NAKAOKI (J. Pharm. Soc. Japan, 1935, 55, 967—978).—EtOH extraction of the flowers yields *cosmosiin* (I), C₂₁H₂₂O₁₁, m.p. 178° (Ac₆ derivative, m.p. 207—208°), hydrolysed (10% H₂SO₄) to glucose and *apigenin*, C₁₅H₁₀O₅, m.p. 347° (triacetate, m.p. 181—182°; no depression with apiin acetate; benzoate, m.p. 210—212°). (I) with MeI yields a substance, m.p. 205—206°, hydrolysed to another substance, m.p. 258—259°, not depressed on admixture with acacetin. With CH₂N₂, (I) yields a glucoside, C₂₃H₂₄O₁₀, m.p. 255°, hydrolysed to *apigenin* Me₂ ether, m.p. 267°. Quercetin and inositol were isolated from the mother-liquors from (I).

CH. ABS. (r)

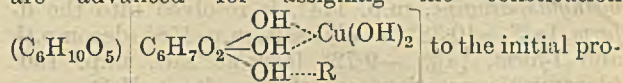
Action of alkalis on araban. T. K. GAPONENKOV (J. Gen. Chem. Russ., 1937, 7, 236—240).—The sp. conductivity of KOH, Ca(OH)₂, or Ba(OH)₂ falls with increasing araban concn., to an extent >, in the case of NaOAc <, and in that of KCl equal to that which would follow from the increase in η ; the p_H of the solutions inversely \propto araban concn. The results are ascribed to formation of non-ionised araban salts. R. T.

Carbohydrates. VIII. Cellulose and its solutions. T. LIESER [with R. EBERT] (Annalen, 1937, 528, 276—295; cf. A., 1936, 592, 595).—The simplest

tetra-alkylammonium bases do not dissolve cellulose (I) but with those of higher mol. wt. the least concn. required for dissolution appears to be a linear function of the mol. wt. Dissolution is observed only within a very narrow limit of concn. above which only swelling occurs. Similar results are recorded with tetra-alkyl-phosphonium and -arsonium bases and with trialkyl-sulphonium and -selenonium bases; as with CsOH the mol. vol. appears to be the controlling factor. Dissolution is regarded as dependent on the formation of mol. compounds. When dialysed against aq. NaOH until the org. bases have been removed (I) remains in solution if >0.6N-NaOH is used. (I) is therefore regarded as fundamentally sol. in dil. NaOH, but a pre-condition for its dissolution is the diminution of micellary arrangement by solvation of all the main valency chains of the micelle. The solubility of (I) in ice-cold, superconc. HCl is thus explained. Addition of MeOH to solutions of (I) in Cu(OH)₂-NH₃ in absence of excess of Cu(OH)₂ gives materials with about 18.5% Cu, whilst if excess of Cu(OH)₂ is present the ppts. contain 22—23% of Cu and 62—64% of (I). There is thus no stoichiometric relationship. Application of the method to hexitols and β -glucosan gives compounds of the annexed type [R = Cu or Cu(NH₃)₄]. The behaviour of (I)



is explained by the hypothesis that more glucose anhydride chains are present on the surface than in the interior of the micelle. This conception of the Cu reaction as a micro-heterogeneous, micellary surface change brings it into line with the pseudo-stoichiometric xanthate reaction. Treatment of (I) with Cu(OH)₂-(CH₂NH₂)₂ yields products containing > the calc. amount of Cu per 2C₆H₁₀O₅. Reasons are advanced for assigning the constitution



duct from (I) and Cu(OH)₂-NH₃ where R = Cu(NH₃)₄(OH)₂/2 and (C₆H₁₀O₅) is the glucose anhydride chain in the interior of the micelle; this passes when heated with MeOH into the substance R = Cu(OH)₂/2. Treatment of regenerated (I) with NaOH and CS₂ gives products with more S than those obtained from (I) and finally leads to a permutoid monoxanthate. Viscose therefore, like (I), has a micellary structure, but the degree of arrangement or density of the micellary packing is < in (I). Absorption of Cu by regenerated (I) is > of (I) and does not increase considerably with time. Action of the Cu-ammine bases on hydrocelluloses therefore appears to be much milder than that of conc. NaOH. H. W.

Preparation of homogeneous forms of soda-cellulose and their importance for the mechanism of mercerisation. III. Soda-cellulose IV. K. HESS and J. GUNDERMANN (Ber., 1937, 70, [B], 527—537).—Treatment of soda-cellulose I (I) with NaOH of diminishing concn. yields products with the interferences of soda-cellulose IV (II) when the NaOH content of the fibres sinks in an unusually marked degree. It is therefore possible that the

cryst. component giving the diagram assigned to (II) is free from alkali and hence not an alkali-cellulose. The characteristic lines of (II) harmonise exactly with those of cellulose III (III) (from cellulose and anhyd. NH_3), but the identity of (II) and (III) is not regarded as established completely. At 100° (I) passes into (II) when 10% NaOH is used whereas at 20° the transformation requires $>6\%$ NaOH. At 100° (II) is converted by 2% NaOH into hydrocellulose (IV) but at 20° it can be preserved for months in presence of 0.5% NaOH. The observation that the introduction of mixed micelles of (II) and (IV) into NaOH of suitable concn. causes a weakening of the intensities of the reflexes of (IV) is regarded as a proof that (II) can be formed synthetically. H. W.

Optical differentiation of different types of cellulose. A. FREY-WISSLING (Mikrochem., Molisch Festschr., 1936, 106—117).—Natural cellulose (I) fibres may be differentiated microscopically from hydrocellulose (II) by their greater refractivity: n_e (= index for extraordinary ray) for (I) $> n$ for NH_2Ph $> n_e$ for (II). Attack by oxidising agents may be detected by its elevation of n_e above 1.600; in conjunction with the Cu no., the presence of either (I) or (II) may thus be unambiguously diagnosed. Esterification leads to a pronounced diminution in both n_e and n_o . The degree of nitration or acetylation may be correlated with the diminution and reversal of sign of the double refraction. J. S. A.

X-Ray studies of wood, lignin, and wood-cellulose.—See A., I, 226.

Optically active amino-acids. [Resolution of *dl*-benzenesulphonyl- α -methylasparagine.] S. BERLINGOZZI and S. DE CECCO (Atti V Congr. Naz. Chim., 1936, 1, 307—310).—*dl*-Benzenesulphonyl- α -methylasparagine, m.p. 174° , is resolved into the *d*-form, $[\alpha]_D^{20} +10.38^\circ$ [brucine salt, m.p. 158° (decomp.)], and *l*-form, $[\alpha]_D^{20} -9.72^\circ$ [brucine salt, m.p. 160° (decomp.)]; rotations are of Na salts in H_2O .

E. W. W.

Scorbamic acid. F. MICHEEL and R. MITTAG (Naturwiss., 1937, 25, 158—159).— α -Deoxy-*l*-ascorbic acid (A., 1936, 706) with PhN_2Cl affords the *phenylhydrazone* of dehydroascorbic acid (I) [not obtained directly from (I) with $\text{NHPh}\cdot\text{NH}_2$], reduced (H_2 -Pd) in neutral or acid solution to *scorbamic acid*, which adds 2 I, reduces cold AgNO_3 , and protects guinea-pigs against scurvy in daily doses of 0.5—1.0 mg.

J. L. D.

Cystine content of insulin.—See A., III, 186.

Behaviour of peptides in aqueous solutions.—See A., I, 240.

Colour reaction between nitroprusside and cysteine. G. SCAGLIARINI (Atti V Congr. Naz. Chim., 1936, 2, 546—547; cf. A., 1929, 160; this vol., 139).—By the action of cysteine hydrochloride on Na nitroprusside and KOH in aq. MeOH a red-violet *ppt.*, $\text{K}_4[\text{Fe}(\text{CN})_5\text{NO}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2]_4\cdot\text{H}_2\text{O}$, is obtained. The reaction is sensitive for cysteine to a dilution of 1:60,000. Cystine and glutathione give the same reaction after reduction. O. J. W.

Action of mercuric sulphate and chloride on cysteine, cystine, cysteinesulphonic acid ($\text{R}\cdot\text{SO}_2\text{H}$), and cysteic acid with reference to the dismutation of cystine. T. F. LAVINE (J. Biol. Chem., 1937, 117, 309—323; cf. A., 1936, 596).—Cysteine (I), cysteic acid (II), and cysteinesulphonic acid (III) are *pptd.* from $2\text{N}\cdot\text{H}_2\text{SO}_4$ by HgSO_4 , the *ppt.* from the last two compounds being sol. in solutions of chlorides. Analytical methods indicate the presence of (I) and (III) (although the latter has not been isolated) in the *ppt.* obtained from cystine (IV)— HgSO_4 — $2\text{N}\cdot\text{H}_2\text{SO}_4$, the dismutative decomp. of (IV) being represented by $2(\cdot\text{SR})_2 + 2\text{H}_2\text{O} = 3\text{RSH} + \text{R}\cdot\text{SO}_2\text{H}$ (cf. *loc. cit.*). Re-formation of (IV) occurs when the Hg has been removed. The optical rotation of solutions of (II), (III), and (IV) in HCl is unaffected by HgCl_2 , but that of (I) is dependent on the amount of HgCl_2 present. According to method of prep. (III) is obtained as a mono-, m.p. 143° (decomp.) or di-, m.p. 146° , -hydrate. H. G. M.

Pyruvic and oxaloacetic cyanohydrins. D. E. GREEN and S. WILLIAMSON (Biochem. J., 1937, 31, 617—618).—On mixing aq. solutions of KCN with AcCO_2H pyruvic acid cyanohydrin (*K* salt, m.p. 87°) is obtained. Oxaloacetic acid cyanohydrin gives a very hygroscopic *K* salt, m.p. 135° (decomp.).

P. W. C.

Compounds of carbamide with magnesium nitrate and sulphate.—See A., I, 256.

Hydrazides of higher unsaturated acids. II. Hydrazide of dehydroundecenoic acid, and its derivatives. A. F. OSKERKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 577—586).—*Et dehydroundecenoate*, b.p. 115 — $120^\circ/3$ mm., and boiling $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ yield *dehydroundecenohydrazide*, m.p. 84 — 85° (hydrochloride, m.p. 134.5° ; compound with COMe_2 , m.p. 75 — 77° ; *Ac* derivative, m.p. 113 — 114°), converted by I in aq. EtOH into *s-didehydroundecenoylhydrazine*, m.p. 131 — 132° . R. T.

Esters of hydroferrocyanic and hydroferri-cyanic acids. J. MEYER, H. DOMANN, and W. MÜLLER (Z. anorg. Chem., 1937, 230, 336—356).—When CH_2N_2 and $\text{H}_4\text{Fe}(\text{CN})_6$ react in Et_2O , the products are $[(\text{CNMe})_4\text{Fe}(\text{CN})_2]$, $[(\text{CNMe})_4(\text{H}_2\text{O})\text{Fe}(\text{CN})_2]\text{CN}$, and an unidentified mixture of substances. The action of CH_2N_2 on $\text{H}_3\text{Fe}(\text{CN})_6$ gives $\text{H}_2[\text{Fe}(\text{CN})_5(\text{CNMe})]$, which forms salts in which H_2 is replaced by Cu, Ni, Zn, or Ag_2 . The compound $\text{Ag}_2\text{Fe}_2(\text{CN})_5(\text{CNMe})_2$ is also described. The corresponding reaction with CHMeN_2 yields $\text{H}_2[\text{Fe}(\text{CN})_5(\text{CNEt})]$, which forms salts in which H_2 is replaced by Ag_2 , Cu, or Ni.

E. S. H.

Two-shell ferrocyanide complex compounds.—See A., I, 241.

Constitution of some additive compounds of tertiary amines and phosphines. K. A. JENSEN (J. pr. Chem., 1937, [iii], 148, 101—106).—The most probable structure of additive compounds of *tert.* phosphines and CS_2 is $\text{S}\cdot\text{C}\cdot\text{P}(\text{R})_3$ (Hantzsch and Hibbert, A., 1907, i, 496), now modified to $\text{P}(\text{R})_3\cdot\text{CSS}\cdot\text{NMe}_3$ and CS_2 yield a compound similarly formulated

as the betaine of HCS_2H . In analogy with the structure assigned by Builmann *et al.* (A., 1935, 331) to the additive products of MeI and betaines, the compound from PET_3 , CS_2 , and MeI is $[\text{PET}_2 \cdot \text{CS}_2 \cdot \text{Me}]^+\text{I}^-$, which is in harmony with its great electrolytic conductivity and the direct titratability of I. The corresponding chloride could not be obtained from PET_3 and ClCS_2Et . The very unstable compounds, $\text{CO}_2\text{Et} \cdot \text{PET}_3\text{Cl}$, $\text{COSEt} \cdot \text{PET}_3\text{Cl}$, $\text{CO}_2\text{Et} \cdot \text{NMe}_3\text{Cl}$, $\text{COSEt} \cdot \text{NMe}_3\text{Cl}$, and $\text{CS}_2\text{Et} \cdot \text{NMe}_3\text{Cl}$ (I), are obtained from their components in well-cooled anhyd. Et_2O . (I) is yellow and at slightly above 0° forms reddish-yellow smeary products with partial reproduction of HCS_2Et and NMe_3 . The remainder are colourless and can be preserved for a short time in complete absence of H_2O , with which they react, e.g., $\text{CO}_2\text{Et} \cdot \text{NMe}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{EtOH} + \text{NMe}_3\text{HCl}$. The instability is explicable when ClCO_2Et and ClCS_2Et are regarded as acid chlorides which with *tert.* amines yield cryst. compounds immediately decomposed by H_2O in the same sense. The condensation of these compounds to cyclic materials in the absence of H_2O does not find its counterpart with the substances now described; $\text{CO}_2\text{Et} \cdot \text{NMe}_3\text{Cl}$ in Et_2O at 35° slowly gives CO_2 , $\text{NMe}_2 \cdot \text{CO}_2\text{Et}$, and, probably, a mixture of NMe_3HCl , NMe_3Cl , and NMe_3EtCl . H. W.

Organic magnesium compounds. V. Reaction between alkyl esters of *p*-toluenesulphonic acid and $\text{OR} \cdot \text{MgX}$. K. MINE (J. Chem. Soc. Japan, 1935, 56, 1112—1117).—The reaction is $2\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_3\text{R}' + 2\text{OR} \cdot \text{MgX} = (\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_3)_2\text{Mg} + 2\text{R}'\text{X} + \text{Mg}(\text{OR})_2$. CH. ABS. (r)

Tri-diamino-salts of cobalt, rhodium, and chromium.—See A., I, 258.

Polarographic study of titano-tartaric complexes.—See A., I, 245.

Dehydrogenation of cyclohexane by sulphide and oxide catalysts. B. MOLDAVSKI, G. KAMUSCHER, and S. LIVSCHITZ (J. Gen. Chem. Russ., 1937, 7, 131—137).—Of a no. of catalysts, Cr_2O_3 had the highest activity and stability at $410\text{--}440^\circ$ (77% yield of C_6H_6 at 434°). The activity of MoS_2 is enhanced by pptn. on SiO_2 gel. R. T.

Desulphuration of organic compounds by catalysis with platinum. N. D. ZELINSKI and E. M. SCHACHNAZAROVA (Bull. Acad. Sci. U.R.S.S., 1936, 563—569).—Pt-C at 350° catalyses both desulphuration and dehydrogenation of mixtures of cyclohexane and mercaptans and org. sulphides, which yield practically pure C_6H_6 after two passages over the catalyst. R. T.

(A) **Phenylcyclopentylethane and cyclopentylcyclohexylethane**, (B) **Phenylcyclopentylpropane and cyclopentylcyclohexylpropane**, and their relation to hydrogenation-dehydrogenation catalysis. J. I. DENISENKO (Bull. Acad. Sci. U.R.S.S., 1936, 577—582, 583—589).—(A) $\text{CH}_2\text{Ph} \cdot \text{CH}_2\text{Cl}$ and cyclopentanone in presence of Mg in Et_2O yield β -1'-hydroxycyclopentylethylbenzene, b.p. $140\text{--}141^\circ/5$ mm., converted by dehydration ($\text{H}_2\text{C}_2\text{O}_4$) into β - Δ^1 -cyclopentenylethylbenzene, b.p. $124\text{--}125^\circ/10$ mm., which gives β -cyclopentylethylbenzene (I), b.p. 255--

256° , with H_2 in presence of Pt-black. (I) and H_2 (Pt-C catalyst at 230°) yield β -cyclopentylethylcyclohexane (II), b.p. $251\text{--}252^\circ$; the reverse reaction takes place when (II) is passed over Pt-C at 290° .

(B) The following substances, prepared as above, react analogously: γ -1'-hydroxycyclopentylpropylbenzene, b.p. $136\text{--}138^\circ/2.5$ mm.; γ - Δ^1 -cyclopentylpropylbenzene, b.p. $117\text{--}118^\circ/3$ mm.; γ -cyclopentylpropylcyclohexane (IV), b.p. $268\text{--}270^\circ$. (I), (II), (III), and (IV) are probably present in petroleum.

R. T.

Decomposition of ethylcyclopentane under conditions of dehydrogenation catalysis. N. D. ZELINSKI and E. M. SCHACHNAZAROVA (Bull. Acad. Sci. U.R.S.S., 1936, 571—576).—Ethylcyclopentane (I) is converted into heptane by H eliminated from cyclohexane (II) when (I)-(II) mixtures are passed over Pt catalyst at $305\text{--}310^\circ$. R. T.

Catalytic cyclisation of aliphatic compounds. I. Cyclisation of aliphatic hydrocarbons in presence of chromic oxide. B. L. MOLDAVSKI, G. D. KAMUSCHER, and M. V. KOBILSKAJA (J. Gen. Chem. Russ., 1937, 7, 169—178).—The following aromatic hydrocarbons were obtained by passing paraffins over Cr_2O_3 at 460° : *o*-85, *m*-2.5, and *p*-xylene 3, and PhEt 10%, from *n*-octane; PhMe, from *n*-heptane; C_8H_8 , from *n*-hexane; *p*-xylene, from Bu_2^2 ; *m*- $\text{C}_6\text{H}_4\text{MePr}^g$, from $(\text{CH}_2\text{Bu}^g)_2$; *o*-xylene, from $\Delta^a + \Delta^b$ -octene, and C_{10}H_8 from PhBu.

R. T.

Substitution reactions of substituted benzenes.—See A., I, 224.

Organic reactions with boron fluoride. XIII. Alkylation of benzene with alcohols. J. F. MCKENNA and F. J. SOWA (J. Amer. Chem. Soc., 1937, 59, 470—471).—Mono-, *p*-di- (with traces of *o*-), and poly-alkylbenzenes are formed from C_6H_6 (1 g.-mol.), AlkOH (1 g.-mol.), and BF_3 (20—65 g.); the ease of reaction is dependent on the ease of dehydration of the AlkOH . The following AlkOH are used: Pr^aOH and Pr^bOH , both yielding Pr^b derivatives; Bu^aOH and *sec*- BuOH , both give *sec*- Bu derivatives; Bu^bOH and Bu^cOH , both afford Bu^c derivatives; cyclohexanol; $\text{CH}_2\text{Ph} \cdot \text{OH}$; allyl alcohol. The alkylating agent is probably the intermediate olefine. H. B.

Chlorination of chlorobenzene in the gaseous phase at $500\text{--}600^\circ$; meta-directing influence of the chlorine atom. J. P. WIBAUT, L. M. F. VAN DE LANDE, and G. WALLAGH (Rec. trav. chim., 1937, 56, 65—70).—The relative proportions of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ in the mixture (I) of $\text{C}_6\text{H}_5\text{Cl}_2$ formed together with a considerable quantity of more highly chlorinated benzenes and some C when excess of PhCl interacts with Cl_2 in presence of pumice at 500° , 550° , and 600° are recorded. (I) contains 50—60% of *m*- $\text{C}_6\text{H}_4\text{Cl}_2$, which exists in only one form, m.p. -24.1° (cf. Kalf, Diss., Amsterdam, 1924). Attempts to repeat the results of Wheeler *et al.* (B., 1933, 421) failed. H. G. M.

Action of nitrogen peroxide on benzene, toluene, and chlorobenzene. I. Nitration in pres-

ence of sulphuric and phosphoric acids. A. I. TITOV and A. N. BARISCHNIKOVA. II. A. I. TITOV (J. Gen. Chem. Russ., 1936, 6, 1801—1805, 1855—1862).—I. PhNO_2 is obtained in 98.4% yield, and of high purity, by adding a solution of 35 g. of N_2O_4 in 100 g. of 94% H_2SO_4 to C_6H_6 at 40—50°. The reaction proceeds with explosive velocity in presence of Hg. PhMe is nitrated similarly, at 0—15°, whilst PhCl is nitrated with saturated $\text{NO}\cdot\text{HSO}_4$, adding oleum during the reaction.

II. The products of reaction of PhMe with gaseous N_2O_4 in diffused daylight, sunlight, or ultra-violet light were $\text{CH}_3\text{Ph}\cdot\text{NO}_2$, $\text{CHPh}(\text{NO}_2)_2$, PhCHO , BzOH , and $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$. R. T.

Preparation of nitrobenzene with maximum specific resistance. L. ZEPALOVA-MICHAILOVA (Trans. Inst. Pure Chem. Reagents, U.S.S.R., 1935, No. 14, 49—57).—The problem is discussed in detail.

CH. ABS. (r)

Preparation of *m*-dinitrobenzene. S. V. SHAH and D. G. PISHAWIKAR (J. Chem. Educ., 1937, 14, 33).—By increasing the proportion of conc. H_2SO_4 , conc. HNO_3 can be used instead of fuming HNO_3 for the nitration of PhNO_2 . 10 g. of PhNO_2 , 15 g. of HNO_3 (*d* 1.41), and 40 g. of conc. H_2SO_4 (*d* 1.82) give an 88% yield of *m*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$. L. S. T.

Colour reactions of the dinitrobenzenes in alkaline solution. R. TRUHAUT (J. Pharm. Chim., 1937, [viii], 25, 216—222; cf. A., 1933, 1314).—Reducing sugars, uric acid, allantoin, and phenyl- β -alanine give colour reactions with only *o*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$. Most NH_2 -acids and the sexual hormones react only with *m*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$ and the simple aldehydes and ketones react with both derivatives. Ninhydrin reacts with both isomerides, each giving characteristic reactions. E. H. S.

Mechanism of reduction of unsaturated compounds with alkali metals and water. C. B. WOOSTER and K. L. GODFREY (J. Amer. Chem. Soc., 1937, 59, 596—597).— PhMe does not react with Na or K in liquid NH_3 ; addition of H_2O causes immediate reaction (? reduction), this being ascribed to the production of nascent H. Use of H_2O to determine excess of Na in reaction media containing liquid NH_3 + PhMe will give misleading results; NH_4Cl (or ammonolysis catalyst) should be used.

H. B.

Preparation and optical rotation of α -phenyl- α -deuteriomethylethane. R. L. BURWELL, jun., F. HUMMEL, and E. S. WALLIS (J. Org. Chem., 1936, 1, 332—335).—*d*- $\text{CH}_2\text{Br}\cdot\text{CHPhMe}$ (cf. J.C.S., 1915, 107, 899) when converted into the Grignard reagent and then treated with D_2O (99.5%) yields *d*- α -phenyl- α -deuteriomethylethane, b.p. 151—152°, $[\alpha]_D^{25} +0.019^\circ$. The smallness of the rotation is in accord with the considerations of Boys (A., 1934, 832), the observed val. being regarded as the upper limit.

H. G. M.

Displacement of bromine from mono- and dibromoethylbenzenes. W. TAYLOR (J.C.S., 1937, 343—351).— α - and β -Bromo- and $\alpha\alpha$ - (from dry HBr and cooled $\text{CPh}\cdot\text{CH}$) and $\alpha\beta$ -dibromo-ethylbenzenes undergo substitution of Br by OEt when heated in dry or aq. (80%) EtOH at 55° for 12—

24 hr. Measurements of increase in acidity show that the reaction is kinetically unimol., and is accelerated by H_2O . This and the high vals. of *P* indicate a composite reaction, with ψ -unimol. formation, and unimol. decomp., of an intermediate oxonium salt. With KOH or NaOEt (0.2*N*) in dry EtOH, α - yields 20%, β - 91%, $\alpha\beta$ - 87% (all independent of temp.), and $\alpha\alpha$ - none, of the corresponding olefine (determined by Br addition in the dark), the reaction being bimol., and accompanied by both uni- and bi-mol. substitution reactions. A. LI.

Relative stability of penta-arylethanes. III. Reversible dissociation of penta-arylethanes.

W. E. BACHMANN and F. Y. WISELOGLE (J. Org. Chem., 1936, 1, 354—382; cf. A., 1933, 943).—Diphenyl-*p*-diphenyl- (I), m.p. 127.5—128°, phenyldi-*p*-diphenyl-, m.p. 145—146.5° and m.p. 70—72° from C_6H_6 -light petroleum, and tri-*p*-diphenyl-, m.p. 207.5—208°, -bromomethane are obtained from the appropriate carbinol (modified or improved prep. described) and $\text{AcBr}\cdot\text{C}_6\text{H}_6$. Only the first two give a Grignard reagent, but in presence of HgBr_2 and $\text{Mg}\cdot\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$, the last gives a double salt $2(\text{C}_6\text{H}_4\text{Ph})_3\text{CBr}\cdot 3\text{MgBr}_2$, decomposed by $\text{KOH}\cdot\text{MeOH}$ to $(\text{C}_6\text{H}_4\text{Ph})_3\text{C}\cdot\text{OMe}$. Interaction of the Grignard reagent from (I) and the appropriate diarylbromomethane (cf. A., 1933, 703) gives α -*p*-diphenyl- $\alpha\alpha\beta$ -tetraphenyl- (II), m.p. 190—192°, and $\alpha\beta$ -di-*p*-diphenyl- $\alpha\alpha\beta$ -triphenyl-, m.p. 180—185°, -ethane, but the following are obtained from the appropriate triarylmethyl-sodium compound and diarylbromomethane: $\alpha\beta\beta$ -tri-*p*-diphenyl- α -di-phenyl-, m.p. 227—230°, $\alpha\alpha$ -di-*p*-diphenyl- $\alpha\beta\beta$ -triphenyl-, m.p. 198—199°, $\alpha\alpha\beta$ -tri-*p*-diphenyl- $\alpha\beta$ -di-phenyl-, m.p. 206—209°, $\alpha\alpha\beta$ -tetra-*p*-diphenyl- α -phenyl-, m.p. 222—228°, $\alpha\alpha\alpha$ -tri-*p*-diphenyl- $\beta\beta$ -di-phenyl-, m.p. 164—167°, $\alpha\alpha\alpha\beta$ -tetra-*p*-diphenyl- β -phenyl-, m.p. 215—220°, $\alpha\alpha\alpha\beta\beta$ -penta-*p*-diphenyl- (III), m.p. 172—185° from $\text{CHCl}_3\cdot\text{EtOH}$ and m.p. 226—234° from C_6H_6 , -ethane. All the foregoing penta-arylethanes as well as pentaphenyl- (IV), β -*p*-diphenyl- $\alpha\alpha\alpha\beta$ -tetraphenyl-, and $\beta\beta$ -di-*p*-diphenyl- $\alpha\alpha\alpha$ -triphenyl-ethane (*loc. cit.*) are cleaved by $\text{AcOH}\cdot\text{HI}$ at 120° giving the corresponding di- and triarylmethanes, and by 40% Na-Hg giving the corresponding di- and tri-arylmethylsodium compounds. No cleavage occurs with 1% Na-Hg. The temp. at which the penta-arylethanes in EtOBz first become coloured due to dissociation into radicals are recorded, and indicate that successive substitution of $\text{C}_6\text{H}_4\text{Ph}$ for Ph progressively weakens the C-C linking. The dissociation is reversible, (IV) being obtained when CPh_3Cl , CHPh_2Br , and Hg are shaken in C_6H_6 , and when CHPh_2Br is shaken in presence of Hg with CPh_3 radicals previously formed from $\text{CPh}_3\text{Cl}\cdot\text{Hg}\cdot\text{C}_6\text{H}_6$, but the position of the equilibrium is almost entirely in favour of the undissociated penta-aryl-ethane. When (II) is refluxed (213°) in EtOBz in N_2 some $(\text{CHPh}_2)_2$ is formed by the irreversible combination of the resulting CHPh_2 radicals. The corresponding $\text{CPh}_2\cdot\text{C}_6\text{H}_4\text{Ph}$ radicals depress the equilibrium concn. of CHPh_2 and hence the rate of disproportionation to $(\text{CHPh}_2)_2$. Similar results were obtained with (IV) and (III), also with other solvents.

The kinetics of the oxidation of (IV) in $o\text{-C}_6\text{H}_4\text{Cl}_2$ by O_2 show that the reaction consists of a relatively slow dissociation into free radicals, which then rapidly combine with O_2 to give the unsymmetrical peroxide as the chief product. In the presence of > 2 mols. of pyrogallol the reaction is strictly of the first order, side reactions are suppressed, and each radical combines with 1 mol. of O , the peroxide radicals being stabilised by the pyrogallol. The heat of activation of dissociation is 27.6 ± 0.5 kg.-cal. The following peroxides were prepared by shaking the appropriate penta-arylethane in $o\text{-C}_6\text{H}_4\text{Cl}_2$ in O_2 : triphenylmethyl benzhydryl, m.p. $93\text{--}94^\circ$, which reacts with $\text{MgMeI}\cdot\text{Bu}^a_2\text{O}$ at 100° to give C_2H_6 and on subsequent hydrolysis $\text{CPh}_3\cdot\text{OH}$ and $\text{CHPh}_2\cdot\text{OH}$; triphenylmethyl phenyl- p -diphenylmethyl, m.p. $129.5\text{--}130^\circ$; triphenylmethyl di- p -diphenylmethyl, m.p. $148\text{--}149^\circ$, decomposed when heated (180° ; 1 hr.; N_2 atm.) into $(p\text{-C}_6\text{H}_4\text{Ph})_2\text{CO}$; di-phenyl- p -diphenylmethyl di- p -diphenylmethyl, m.p. 161° (decomp.); phenyldi- p -diphenylmethyl benzhydryl, m.p. $151\text{--}152^\circ$; tri- p -diphenylmethyl phenyl- p -diphenylmethyl, m.p. 168° . The structures of these peroxides were confirmed by cleavage with 2% $\text{Na}\text{--}\text{Hg}$, hydrolysis of the resulting products giving the di- and tri-arylcabinols corresponding with the di- and tri-arylmethyl radicals. With H_2SO_4 the peroxides give colours characteristic of the sulphates of these cabinols.

H. G. M.

Exchange of sulphonyl groups. D. T. GIBSON and J. D. LOUDON (J.C.S., 1937, 487—489).—The equilibrium point in the reaction $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{SMe} + \text{R}\cdot\text{SO}_2\text{Na} \rightleftharpoons \text{R}\cdot\text{SO}_2\cdot\text{SMe} + \text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\text{Na}$ was approx. determined for a series of 14 sulphates by mixing the reactants in aq. EtOH or aq. EtOH -dioxan solution and observing the rotation. The weaker sulphonyl anion retains the greater hold on the thioaryl group. Change of solvent changes the endpoint, but substitution of Me by $2:5\text{-C}_6\text{H}_3\text{Cl}_2$ has little effect. The exchange equilibrium (ester type) $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{SMe} + \text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_3\text{Cl}_2 \rightleftharpoons$ can be displaced by excess of reactant or product. Reaction of $\text{R}\cdot\text{SO}_2\cdot\text{CH}(\text{Salk})\cdot\text{COMe}$ or $1:2:4\text{-R}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ with sulphinate ions is obscured by side-reactions. With $2:5\text{-C}_6\text{H}_3\text{Cl}_2\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_3\text{Cl}_2$ in EtOH , Na camphorsulphinate (I) gives the camphor-thiolsulphinate, m.p. $121\text{--}122^\circ$, $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\text{Na}$ the 4-chlorobenzenethiolsulphinate, m.p. $121\text{--}122^\circ$, and $1:3:4\text{-SO}_2\text{Na}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe}$ the 4-methoxy- m -toluene-thiolsulphinate, m.p. 96° , of $2:5$ -dichlorophenyl. $1:2:4\text{-C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ and (I) in hot EtOH yield $2:4$ -dinitrophenyl 10-camphoryl sulphone, m.p. 168° , $[\alpha]^{18}_{\text{D}} +161\text{--}165^\circ$ in dioxan.

A. LI.

Volatile plant substances. V. Preparation of the fundamental substance of the azulene series. P. A. PLATTNER and A. S. PFAU (Helv. Chim. Acta, 1937, 20, 224—232; cf. A., 1936, 993).—cyclopentenocycloheptanone is hydrogenated (Ni in EtOH) to cyclopentanocycloheptanone, which is reduced by Na and EtOH to cyclopentanocycloheptanol, b.p. $126\text{--}128^\circ/10$ mm., dehydrogenated by $\text{Pd}\text{--}\text{C}$ at $300\text{--}350^\circ$ to azulene (dicyclo-[0.3.5]- $\Delta^{1:3:5:7:9}$ -decapentaene) (I), m.p. $98.5\text{--}99^\circ$. Isolation of (I) is effected by fractional sublimation of its additive

product (II), m.p. $166.5\text{--}167.5^\circ$, with $\text{C}_6\text{H}_3(\text{NO}_2)_3$, or, preferably, by treatment of (II) with Al_2O_3 in presence of C_6H_6 -cyclohexane. The analogous compound, m.p. $99.5\text{--}100^\circ$, with $2:4:6\text{-C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ is described. (I) dissolves readily in conc. mineral acids and is repptd. by immediate addition of H_2O but is relatively unstable in solution. (I) has a marked odour of C_{10}H_8 , which appears to be proper to it since mixtures of (II) and the corresponding compound of C_{10}H_8 are readily separable. Small amounts of (I) appear to be formed during the dry distillation of Ca adipate, apparently owing to the presence of a dehydrogenating reagent. The utility of the chromatographic method is illustrated further by the isolation of S -guaiazulene from its picrate or compound with $\text{C}_6\text{H}_3(\text{NO}_2)_3$ and of vetivazulene from its picrate.

H. W.

Mechanism of reaction of destructive hydrogenation of tetrahydronaphthalene. S. B. ANISIMOV and V. F. POLOZOV (J. Gen. Chem. Russ., 1936, 6, 1847—1854).—The products of hydrogenation in presence of $\text{SiO}_2\cdot\text{WO}_3$ catalyst at $420\text{--}480^\circ$ are successively, PhBu^a , PhPr^a , PhEt , and PhMe . The same process takes place with catalysts containing halogen (VCl_4 , AlCl_3 , I , HgCl_2 , BiCl_3), except that part of the PhBu^a formed isomerises to $\text{C}_6\text{H}_5\text{Me}_2$.

R. T.

Polymerisation of tetrahydronaphthalene. H. I. WATERMAN, J. J. LEENDERTSE, and J. B. NIEMAN (Rec. trav. chim., 1937, 56, 59—64).—Polymerisation of tetrahydronaphthalene at 50° in presence of AlCl_3 gives products the physical consts. of which indicate that opening and closing of rings has occurred to a slight extent. A substance, m.p. 72° , probably an anthracene or phenanthrene derivative, has been isolated (cf. Schroeter, A., 1925, i, 125).

H. G. M.

Derivatives of 4-iodonaphthalene-1-sulphonic acid. H. GOLDSTEIN, T. BLEZINGER, and H. FISCHER (Helv. Chim. Acta, 1937, 20, 218—220).—Diazotisation of $1:4\text{-NH}_2\text{-C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ and treatment of the product with NaI gives Na 4-iodonaphthalene-1-sulphonate ($+1\text{H}_2\text{O}$) [corresponding Ba , Ag (I), and anilinium, m.p. 308° (corr.), salts]. (I) is transformed by EtI in boiling anhyd. C_6H_6 into Et 4-iodonaphthalene-1-sulphonate, m.p. 102° (corr.); the Me ester has m.p. 113° . The m.p. of the chloride, amide, and anilide are 124.5° (corr.), 206.5° (corr.), and 136.5° (corr.), respectively.

H. W.

Dinaphthylsulphonic acids. W. M. CUMMING and G. D. MUIR (J. Roy. Tech. Coll., 1937, 4, 61—71).—The Na or K salts of $1:4$ -chloro-, $1:2$ - and $2:1$ -bromo-, $1:2$ - (sulphonamide, m.p. 247°), $1:4$ -, $1:5$ -, $1:8$ -, $2:1$ -, and $2:6$ -iodo-naphthalenesulphonic acids were boiled with Cu powder and a little CuSO_4 . The $2:1$ -Br- and -I-compounds yielded salts of $2:2'$ -dinaphthyl- $1:1'$ -disulphonic acid $[(\text{NH}_4)_2]$ salt m.p. $303^\circ\text{--}304^\circ$; disulphonyl chloride, m.p. $245\text{--}246^\circ$ (decomp.); $1:8$ -iodo- gave (probably) Na_2 $1:1'$ -dinaphthyl- $8:8'$ -disulphonate, which was decomposed by PCl_5 , but with $\text{NH}_2\text{Ph}\cdot\text{HCl}$ gave $1:1'$ -dinaphthyl- $8:8'$ -sultone, m.p. 252° (decomp.); $1:2$ - and $1:4\text{-C}_{10}\text{H}_6\cdot\text{I}\cdot\text{SO}_3\text{H}$ merely lost their halogen, while the remainder did not react. In another

series, 1:2-, 1:4-, 1:8-, 2:6-, and 2:1-diazonaphthalenesulphonic acids were treated with $\text{NH}_3\text{-Cu}_2\text{O}$ (reduced by NH_2OH); the last-named afforded the dinaphthyldisulphonate, the remainder giving azonaphthalenedisulphonic acids of the Ciba Orange type.

A. Li.

Nitration of polycyclic aromatic hydrocarbons by means of nitrous fumes. (SIGNA.) L. MONTI (Atti V Congr. Naz. Chim., 1936, 1, 407—410).—Nitrous fumes convert acenaphthene in Et_2O into the 5- NO_2 - and in C_6H_6 or AcOH at room temp. into the 5:6-(NO_2)₂-derivative. Fluorene at room temp. gives only the 2- NO_2 , but at 80—90° a mixture of the 2:7- and 2:5-(NO_2)₂-derivatives. Ph_2 does not react at room temp., but at 90° yields the 4- NO_2 - and, slowly, the 4:2'-(NO_2)₂-derivative.

E. W. W.

Destructive hydrogenation of octahydroanthracene and -phenanthrene. E. I. PROKOPETZ (J. Appl. Chem. Russ., 1937, 10, 126—130).—The products of hydrogenation (485—490°/100 atm.) of octahydro-anthracene (I) or -phenanthrene (II) or 7-methyl-1:2:3:4-tetrahydronaphthalene (III) are *m*- and *p*-xylene. The reaction is believed to consist of (I) or (II) \rightarrow (III) \rightarrow *m*- and *p*-xylene.

R. T.

Reaction of alkali metals with polycyclic hydrocarbons: 1:2-benzanthrene, 1:2:5:6-dibenzanthrene, and methylcholanthrene. W. E. BACHMANN (J. Org. Chem., 1936, 1, 347—353).—1:2-Benzanthracene (I) (obtained in 54% yield by heating $1\text{-C}_{10}\text{H}_7\text{-CO-C}_6\text{H}_4\text{Me-o}$ with Zn at 410°) when treated with $\text{Na-Hg-C}_6\text{H}_6\text{-Et}_2\text{O}$ gives a blue solution which turns rose-red; subsequent addition of MeOH gives 9:10-dihydro-1:2-benzanthracene, m.p. 112—112.5° (dipicrate, m.p. 139—139.5°), dehydrogenated by S to (I) and oxidised by $\text{CrO}_3\text{-AcOH}$ to 1:2-benz-9:10-anthraquinone. Similarly 1:2:5:6-dibenzanthracene (II) gives a solution which changes from green to blue and with MeOH gives 9:10-dihydro-1:2:5:6-dibenzanthracene, m.p. 218.5—219.5° [dipicrate, m.p. 221—222° (decomp.) according to method of heating] (cf. A., 1934, 180), dehydrogenated by S to (II) and oxidised to the corresponding 9:10-anthraquinone. 20-Methylcholanthrene (III) (for numbering see A., 1935, 1117), m.p. 180.3—180.6° [prepared by pyrolysis of 4-(1-naphthoyl)-7-methylindane, m.p. 82.7—83.5° (cf. A., 1935, 853)], with $\text{Na-C}_6\text{H}_6\text{-Et}_2\text{O}$ gives a purple solution which with MeOH gives 11:14-dihydro-20-methylcholanthrene, m.p. 136—137°, dehydrogenated by S to (III) and oxidised to 6-methyl-1:2-benzanthraquinonyl-5-acetic acid (A., 1934, 656). Similar reactions occur with $\text{Li-C}_6\text{H}_6\text{-Et}_2\text{O}$; in each case, however, the colour of the resulting solution was blue.

H. G. M.

Polycyclic aromatic hydrocarbons. XV. New homologues of 1:2-benzanthracene. J. W. COOK, A. M. ROBINSON, and F. GOULDEN (J.C.S., 1937, 393—396).—5-Ketododecahydro-1:2-benzanthracene with MgEtBr , followed by dehydration (KHSO_4) and dehydrogenation (Pt-black) of the carbinol, yields 5-ethyl-1:2-benzanthracene, m.p. 120° (picrate, m.p. 150—151°), oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$) to 5-ethyl-1:2-benzanthraquinone, m.p. 97—98°. *o*-1-Naphthoyl-

benzoic acid and MgMeI yield (1-naphthyl)methylphthalide, m.p. 152—153°, reduced (after hydrolysis) by Zn dust to *o*- α -(1-naphthyl)ethylbenzoic acid, m.p. 167—168°; cyclisation (anhyd. ZnCl_2) gives an anthrone, which is reduced ($\text{Zn} + \text{NaOH}$) to 9-methyl-1:2-benzanthracene, m.p. 138—139° (picrate, m.p. 115—116°). β -*o*-Tolylethylchloride, b.p. 100°/15—20 mm. (from the alcohol by SOCl_2 and NPhMe_2), reacts in the form of a Grignard reagent with *trans*-2-ketodecahydronaphthalene to give 2-(β -*o*-tolylethyl)-*trans*-2-decahydronaphthol, b.p. 170—180°/0.6 mm. (crystallises slowly at 0°), which is dehydrated (KHSO_4) to 2-(β -*o*-tolylethyl)- $\Delta^{3:3}$ -octahydronaphthalene, b.p. 160—162°/0.7 mm.; this is cyclised by AlCl_3 in CS_2 to 4'-methyl-dodecahydro-1:2-benzanthracene, m.p. 92.5—93.5°, which with Se at 300° yields 4'-methyl-1:2-benzanthracene, m.p. 194—195° (picrate, m.p. 139—140°), oxidised to 4'-methyl-1:2-benzanthraquinone, m.p. 219—220°. 10-Methyl-1:2-benzanthracene was synthesised from 1:2-benz-10-anthrone and MgMeI , the carbinol being treated with picric acid, followed by Na_2CO_3 .

A. Li.

Preparation of dibenzpyrene. G. B. ZILBERMAN (J. Gen. Chem. Russ., 1937, 7, 234—235).—1:2:6:7-Dibenzpyrene-3:8-quinone is reduced by HI and red P at 190—200° (14 hr.) to 1:2:6:7-dibenzpyrene, m.p. 320—320.5°.

R. T.

Oxidation of rubrene in light.—See A., I, 255.

Carcinogenic hydrocarbons. I. 15:20-Dimethylcholanthrene. W. F. BRUCE [with L. F. FIESER] (J. Amer. Chem. Soc., 1937, 59, 479—480).—A mixture (prep. as Bachmann *et al.*, A., 1936, 326) of 4-bromo-2:7-dimethyl-, b.p. 115—117°/0.15 mm., and 7-bromo-2:4-dimethyl-hydrindone, m.p. 81°, is reduced (Clemmensen) to 4-bromo-2:7-dimethylhydrindene, b.p. 104—106°/2.5 mm., the Grignard reagent from which with $\alpha\text{-C}_{10}\text{H}_7\text{-COCl}$ gives 4- α -naphthoyl-2:7-dimethylhydrindene (I), b.p. 200°/1 mm., m.p. 80—81°, and some 2:4-dimethylhydrindene, b.p. 105—106°/25 mm. (I) heated at 405—410°/30 min. affords poor yields of 15:20-dimethylcholanthrene, m.p. 134—136°, and (mainly) 20-methylcholanthrene (for numbering see A., 1935, 1117).

H. B.

Synthesis of 5:6-(3'-methylcyclopenteno)retene, a compound structurally related to Diels' hydrocarbon. D. E. ADELSON and M. T. BOGERT (Proc. Nat. Acad. Sci., 1937, 23, 117—119).—The synthesis of 5:6-(3'-methylcyclopenteno)-1-methyl-7-isopropylphenanthrene (I), m.p. 74.5—75.5° (corr.), is outlined through the following stages; 6-acetylretene R-COMe ($\text{R} = \text{C}_{13}\text{H}_{17}$) + $\text{Zn} + \text{CH}_2\text{Br-CO}_2\text{Et} \rightarrow \text{OH-CRMe-CH}_2\text{-CO}_2\text{H} + \text{Ac}_2\text{O} + \text{NaOAc} \rightarrow \text{CRMe-CH-CO}_2\text{H} + \text{Na-Hg} \rightarrow \text{CHRMMe-CH}_2\text{-CO}_2\text{H} \rightarrow \text{CHRMMe-CH}_2\text{-CO-Cl} + \text{AlCl}_3 \rightarrow \text{C}_{18}\text{H}_{16} \begin{smallmatrix} \text{CHMe} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CH}_2 + \text{Zn-Hg-HCl} \rightarrow \text{(I)}$. No details are given.

J. W. B.

Decomposition of aryldithiocarbamates. N. S. DROZDOV (J. Gen. Chem. Russ., 1937, 7, 185—187).—The reactions $\text{NHR-CS}_2\text{M}$ (I) \rightarrow $\text{CS(NHR)}_2 + \text{H}_2\text{S}$; 2(I) \rightarrow NHR-CS-NH_2 (II) + M_2CS_3 ; (I) \rightarrow $\text{R-NCS} \rightarrow$ (II) ($\text{R} = \text{Ph}$, *o*-tolyl; $\text{M} = \text{NH}_3$, Cu) take place

when (I) is heated in aq. solution in presence of $(\text{NH}_4)_2\text{CO}_3$, whilst in presence of excess of Cu^{++} the chief product is $\text{R}\cdot\text{NCS}$. R. T.

Condensations of aromatic amines with formaldehyde in media containing acid. IV. Conversion of diarylaminomethanes into substituted dihydro- and tetrahydro-quinazolines in non-aqueous media. J. K. SMONS (J. Amer. Chem. Soc., 1937, 59, 518—523).—Di-*p*-toluidinomethane (I), $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ (II), and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2\cdot\text{HCl}$ at 60—90° in absence of solvent give (according to proportions of reagents used) varying amounts of *o*-amino-*m*-xylyl-*p*-toluidine [*p*-tolyl-(2-amino-5-methylbenzyl)amine] (III), 3-*p*-tolyl-6-methyl-1:2:3:4-tetrahydro- (IV) and 3:4-dihydro- (V)-quinazoline, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHMe}$ (VI). The production of (IV) and (V) probably occurs thus: (III) + (I) \rightarrow (IV) + (II) (2 mols.); (IV) + (I) \rightarrow (V) + (II) + (VI). Thus, (I) and (III) in EtOH give (IV) (86.3%) and (II) (60.5%). (IV) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2\cdot\text{HCl}$ in EtOH afford (V), (VI), and 2:2'-diamino-5:5'-dimethyldiphenylmethane (*dibenzylidene* derivative, m.p. 186°), whilst (I), (IV), and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2\cdot\text{HCl}$ in EtOH yield (V) and (VI). (V) is also obtained by oxidation (KMnO_4 , COMe_2) of (IV). (IV) is cleaved by BzCl in $\text{C}_5\text{H}_5\text{N}$ to give the Bz_2 derivative, m.p. 190.2—190.5°, of (III). Di-*p*-phenetidinomethane and $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$ at 100° (bath) afford 6-ethoxy-3-*p*-phenetyl-3:4-dihydroquinazoline, m.p. 141—142° [reduced (Na, EtOH) to the 1:2:3:4- H_4 -derivative, m.p. 143—143.5°], and $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$. H. B.

Rearrangement of alkylanilines. VII. Behaviour of alkylanilines with *tert.* alkyl groups. W. J. HICKINBOTTOM (J.C.S., 1937, 404—406; cf. A., 1935, 76).— NHPhBu^x , or its hydrochloride, when heated with CoCl_2 at 212° under conditions allowing escape of volatile products, gives much *iso*- C_4H_8 and only 1% of $p\text{-C}_6\text{H}_4\text{Bu}^x\cdot\text{NH}_2$. *tert.*-Hexylaniline gives similarly much $\text{CHMe}\cdot\text{CMeEt}$ and only 2—4% of *sec.* amine. Formation of $p\text{-C}_6\text{H}_4\text{X}\cdot\text{NH}_2$ ($\text{X} = \text{alkyl}$) from NH_2Ph and olefine in presence of promoters is thus a direct union and not a secondary reaction due to rearrangement of the *sec.* amine. R. S. C.

Catalytic condensation of acetylene with toluidines. N. S. KOZLOV and J. D. MOGILANSKI (J. Gen. Chem. Russ., 1936, 6, 1897—1901).—*o*-Toluidine in PhMe and C_6H_6 in presence of CuCl yield *trans*-diethylidene-*o*-toluidine, 2:8-dimethylquinoline, $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHEt}$, and dimethyltetrahydroquinoline. With *p*-toluidine, the products are *trans*-diethylidene-*p*-toluidine ($\beta\gamma$ -di-*p*-tolylamino- Δ^8 -butene), m.p. 140°, and 2:6-dimethylquinoline; *m*-toluidine gives 2:7-dimethylquinoline. It is supposed that diethylidenetoluidines are in all cases intermediate products in the production of methylquinolines. R. T.

Action of amines on semicarbazones. A. B. CRAWFORD and J. PRIMROSE (J. Roy. Tech. Coll., 1937, 4, 28—31).—The reaction of semicarbazones with NH_2R is restricted if R is electronegative. Acetonesemicarbazone (I), heated with *o*-anisidine, gives acetone- δ -*o*-anisylsemicarbazone, m.p. 143—144°, hydrolysed to δ -*o*-anisylsemicarbazide hydrochloride,

m.p. (decomp.) 179—180°. The free base melts at 144—145° (*benzylidene* derivative, m.p. 178°). With $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ or NH_2Bz (I) undergoes thermal decomp. without condensing, and with Et oxamate it gives dimethylketazine, urazole, oxamide, and EtOH.

A. LI.

Some substituted anilines. A. MANGINI (Atti V Congr. Naz. Chim., 1936, 1, 395—402).—1:3:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ (cf. A., 1935, 855) and the appropriate amines yield 5-chloro-2-nitroallylaniline, m.p. 52—53°; 5-chloro-2-nitro-3'-methyl-diphenylamine, m.p. 192—193° (decomp.); the corresponding 4'-*Me* derivative (I); 5-chloro-4'-bromo-2-nitrodiphenylamine (II), m.p. 161—162°; 4-(5'-chloro-2'-nitroanilino)-diphenyl (III), m.p. 138—139°; 5-chloro-2-nitro-3'-, m.p. 143—144° (decomp.), and 4'-hydroxydiphenylamine, m.p. 142—143°; 5-chloro-2-nitrodiphenylamine-3'-, m.p. 240—241°, and 4'-carboxylic acid, m.p. 270—272° (decomp.); and 2-(5'-chloro-2'-nitroanilino)-pyridine, m.p. 153—154°. $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ gave no positive reaction, nor did *o*-, *m*-, or *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$; $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, however, gives 5-chloro-2:4'-dinitrohydrazobenzene, m.p. 190.5—192°, converted by Ac_2O into 5-chloro-2-*p*-nitrophenyl-2:1:3-benzotriazole 1-oxide, m.p. 143—144°. (I), (II), and (III) are converted by HNO_2 into 6-chloro-1-*p*-tolyl-, m.p. 239—241°, 1-*p*-bromophenyl-, m.p. 209—210°, and 1-*p*-diphenyl-1:2:3-benzotriazole, m.p. 175—176°, respectively. (I) and (II), and especially *NN'*-bis-(5'-chloro-2'-nitrophenyl)benzidine (*loc. cit.*), are sensitive reagents for HNO_2 and HNO_3 ; other colour reactions are tabulated. E. W. W.

Diphenyl and its derivatives. XV. Passage from the diphenyl to the fluorene system. L. MASOARELLI (Gazzetta, 1936, 66, 843—850).—A review of previous work. Diazotised 2-amino-2'-methyl-diphenyls, when decomposed by H_2O , generally give fluorenes, except when further substituted in both the 6 and 6' positions; when one of these positions is substituted, the yield of the fluorene is low. E. W. W.

Manufacture of quaternary ammonium compounds.—See B., 1937, 215.

Compounds of cyclic diamines with metallic salts. Zinc salts. R. CERNATESCO and (MLLE.) M. PONT (Ann. Sci. Univ. Jassy, 1935, 21, 393—406).—The prep. of $\text{ZnCl}_2\cdot\text{Tm}$, $\text{ZnCl}_2\cdot\text{Tp}$, $\text{ZnBr}_2\cdot\text{Tm}$ (Tm , $\text{Tp} = m$ - and *p*-tolylenediamines), $\text{ZnCl}_2\cdot 2\text{N}$, $\text{ZnI}_2\cdot 2\text{N}$, $\text{ZnBr}_2\cdot 2\text{N}$, $\text{ZnCl}_2\cdot \text{N}$ [$\text{N} = \text{C}_{10}\text{H}_6(\text{NH}_2)_2$] is described. By Hieber's method (A., 1929, 691) of displacement of the base by NH_3 , it is established that in $\text{ZnCl}_2\cdot 2\text{N}$, $\text{ZnBr}_2\cdot 2\text{N}$, $\text{Cd}(\text{NO}_3)_2\cdot 2\text{N}$, $\text{Cu}(\text{NO}_3)_2\cdot 2\text{N}$, $\text{ZnBr}_2\cdot\text{Tm}$, and $\text{ZnCl}_2\cdot\text{Tp}$, both NH_2 in each mol. of base are bound to the salt mols. by one co-ordinate linking, whereas in $\text{ZnCl}_2\cdot\text{Tm}$ only one is so bound. R. C. M.

Complex salts of the racemic and optically active diaminocyclohexane with tervalent cobalt and rhodium.—See A., I, 259.

Peculiar type of crystal growth of certain 3-benzamido-4-methoxy-*o*-toluidine derivatives. V. A. IZMAILSKI and V. I. STAVROVSKAJA (J. Gen. Chem. Russ., 1937, 7, 80—83).—The following

substances crystallise from org. solvents in curved, spirally propagating needles: 2-*p*-nitrobenzamido-, m.p. 286°, -*p*-nitrobenzylideneamino-, m.p. 193°, -β-hydroxynaphthaleneazo-, m.p. 231—232° (decomp.), and -*p*-dimethylaminobenzeneazo-3-benzamido-4-methoxytoluene, m.p. 172—172.5°. R. T.

Thioformylation of amines. A. R. TODD, F. BERGEL, KARIMULLAH, and R. KELLER (J.C.S., 1937, 361—364).—HCS₂H (I) and MeCS₂H with PhNCO or PhNCS yield thio-form- and -acet-anilide, respectively. From (I) or HCS₂K, and the appropriate amine, thioformyl derivatives of the following are obtained; 6-aminoquinoline, m.p. 236°, tryptamine, m.p. 82°, mescaline, m.p. 92°, *o*-C₆H₄(NH₂)₂, m.p. 77° (unstable; slowly transformed into benzimidazole), *o*-NH₂·C₆H₄·NHAc, m.p. 173°, NH₂·CH₂·Ph, m.p. 64°, NH₂·CH₂·C₆H₄·NO₂-*o*, m.p. 94°. With HCS₂K, *o*-NH₂·C₆H₄·CH₂·NH₂ affords dihydroquinazoline, and (CH₂·NH₂)₂ gives ethylenebisthioformamide, m.p. 146—147°. isoAmylamine and (I) give *N*-isoamylthioformamide, b.p. 143—146°/10 mm., which, treated successively with CH₂BzBr and picric acid, affords 4-phenyl-3-isoamylthiazolium picrate, m.p. 101°. An improved prep. of thioformamide from HCS₂K and aq. NH₃ is described. J. D. R.

Auxo-enoid systems. IV. The colour of nitrobenzoyl derivatives of aromatic amines. V. A. ISMAILSKI and B. M. BOGOSLOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 17—22).—The absorption curves of *N*-(4-nitrobenzoyl)-*N*-benzyl-*p*-aminophenol (I), pale yellow, m.p. 180—181°, -*p*-phenetidine (II), yellow, m.p. 101—102°, and *N'*-(4-nitrobenzoyl)-*N'*-benzyl-*NN'*-dimethyl-*p*-phenylene-diamine, red, m.p. 118—119°, have been measured in order to provide further support for the theory that their colour is not due to tautomerism between ·CO·NH· and ·C(OH)·N· (A., 1936, 1396), which is prevented by CH₂Ph, but is due to the direct action of the nitro-enoid system on the auxo-enoid system in the same mol. Compared with *p*-NO₂·C₆H₄·CO·NHPh (I) and (II) show bathochromic displacement of the absorption band, as does also (II) compared with NHBz·C₆H₄·NMe₂. The absorption maxima at 270 Å. approx. coincide with that for NHBzPh, thus demonstrating that in the latter substance it cannot be due to ·C(OH)·N·. K. H. S.

Heterocyclic compounds containing nitrogen. XXVI. Preparation of *o*-aminated *p*-phenylene-diethylamines (*p*-di-β-aminoethylbenzenes). P. RUGGLI and W. MÜLLER (Helv. Chim. Acta, 1937, 20, 189—198).—*p*-Phenylenediethylamine sulphate (I), m.p. (indef.) 210°, in conc. H₂SO₄ is converted by HNO₃ (*d* 1.52) and conc. H₂SO₄ into 2-nitrophenylene-1:4-diethylamine sulphate, transformed by BzCl and NaOH into the 2-nitro-1:4-di-β-benzamidoethylbenzene, m.p. 184—185°. This is reduced (Ni in H₂O-EtOH-EtOAc) to 2-amino-1:4-di-β-benzamidoethylbenzene, m.p. 201°, which does not afford a cryst. Bz derivative but is transformed by Ac₂O into 2-acetamido-1:4-di-β-benzamidoethylbenzene (II), m.p. 176°. (II) with HNO₃ (*d* 1.52) at -15° to -5° affords 5-nitro-2-acetamido-1:4-di-β-benzamidoethylbenzene, decomp. about 150°, reduced to 5-amino-2-acetamido-1:4-di-β-benzamidoethylbenzene, whence 2:5-diacetamido-

1:4-di-β-benzamidoethylbenzene (III), m.p. 285°. Mild hydrolysis of (III) with EtOH-HCl affords 2:5-diacetamido-1:4-di-β-aminoethylbenzene dihydrochloride, decomp. 245—250°, whereas with HCl (*d* 1.19) at 120° it gives 2:5-diamino-1:4-di-β-aminoethylbenzene tetrahydrochloride, decomp. about 300—305°. Attempts to effect ring-closure to a pyrrolidine derivative were unsuccessful. Gradual addition of (I) to HNO₃ (*d* 1.52) and conc. H₂SO₄ at 80—100° gives 2:6-dinitrophenylene-1:4-diethylamine disulphate, darkens at 250°, whence 2:6-dinitro-1:4-di-β-benzamidoethylbenzene, m.p. 216—218°, 2:6-diamino-, m.p. 214°, and 2:6-diacetamido-, m.p. 268—270°, -1:4-di-β-benzamidoethylbenzene. The last-named substance is hydrolysed to 2:6-diaminophenylene-1:4-diethylamine tetrahydrochloride, m.p. 275° (decomp.), with which ring-closure could not be effected. *p*-C₆H₄(CH₂·CN)₂, *p*-NO₂·C₆H₄·NMe₂, and NaOH in EtOH give the anil *p*-C₆H₄[C(CN)·N·C₆H₄·NMe₂]₂, m.p. 240°, hydrolysed to *p*-C₆H₄(CO₂H)₂ and HCN. Oxidation of the "polymeric nitrile" [obtained by the action of KCN on *p*-C₆H₄(CH₂Br)₂] by KMnO₄ in alkaline solution yields *p*-C₆H₄(CO₂H)₂. H. W.

Diphenyl series. VII. New derivatives. VIII. Bromination of 2-nitro-4'-amino- and 4-nitro-2'-amino-diphenyl. V. BELLAVITA (Atti V Congr. Naz. Chim., 1936, 1, 290—295, 296—306).—VII. 4-Nitro- is reduced to 4-amino-2:4'-diacetamidodiphenyl, m.p. 233—234° (2:4:4'-triacetamidodiphenyl, m.p. 309—311°), from which the Ac₂ derivative, m.p. 225°, of 4-bromo-2:4'-diaminodiphenyl, m.p. 102° (hydrochloride, m.p. 285°), is obtained. 3'-Nitro- is reduced to 3'-amino-2:4'-diacetamidodiphenyl, m.p. 296—302° (2:3':4'-triacetamidodiphenyl, m.p. 288—290°), which on diazotisation and treatment with CuBr gives 2:4'-diacetamido-3'-hydroxydiphenyl, m.p. 258°. 2:4'-Diaminodiphenyl is brominated in AcOH to 3:5:3':5'-tetrabromo-2:4'-diaminodiphenyl, m.p. 186° (Ac₂ derivative, m.p. 155°), converted by diazotisation and H₃PO₂ into 3:5:3':5'-tetrabromodiphenyl. 4:3'-Dinitro-2:4'-diaminodiphenyl diazotised and treated with Hg(NO₃)₂ and KCl or KBr gives 2:4'-dichloro-, m.p. 142°, and 2:4'-dibromo-4:3'-dinitrodiphenyl, m.p. 141°. The corresponding 5:3':(NO₂)₂-compound is similarly converted into 2:4'-dibromo-5:3'-dinitrodiphenyl, m.p. 170°.

VIII. 2-Nitro-4'-aminodiphenyl is brominated in AcOH to 4:5-dibromo-2-nitro-4'-aminodiphenyl (I), m.p. 141° (Ac derivative, m.p. 182—183°), reduced to 4:5-dibromo-2:4'-diaminodiphenyl, m.p. 108—109° (Ac₂ derivative, m.p. 245°, also obtained from 4'-bromo-2:4'-diacetamidodiphenyl). The last diazotised gives with H₃PO₂ 3:4-dibromodiphenyl, new m.p. 42°; (I) similarly gives 4:5-dibromo-2-nitrodiphenyl, m.p. 108°, reduced to 4:5-dibromo-2-aminodiphenyl, m.p. 86° [hydrochloride, m.p. 215° (decomp.)]; Ac derivative, m.p. 151—152°. This is converted (HNO₂ and CuBr) into 2:4:5-tribromodiphenyl, m.p. 68°. (I) similarly gives 4:5:4'-tribromo-2-nitrodiphenyl, m.p. 144°, reduced to 4:5:4'-tribromo-2-aminodiphenyl (II), m.p. 113° (Ac derivative, m.p. 189—190°), from which, or from 4:5-dibromo-2:4'-diaminodiphenyl, 2:4:5:4'-tetrabromodiphenyl,

m.p. 135°, is obtained. (II) is diazotised and reduced (H_2PO_2) to 4:5:4'-tribromodiphenyl, m.p. 102°. 4'-Nitro-2-aminodiphenyl is similarly brominated to 3:4-dibromo-4'-nitro-2-aminodiphenyl (III), m.p. 189° (Ac derivative, m.p. 158°), converted into 3:4-dibromo-2:4'-diaminodiphenyl, m.p. 105° (Ac₂ derivative, m.p. 108°) (again converted into 3:4-dibromodiphenyl), into 3:4-dibromo-4'-nitrodiphenyl, m.p. 160°, 3:4-dibromo-4'-aminodiphenyl, m.p. 114° (Ac derivative, m.p. 217—218°) (again converted into 4:5-dibromo- and into 4:5:4'-tribromo-diphenyl), and into 2:3:4-tribromo-4'-nitrodiphenyl, m.p. 148°, reduced to 2:3:4-tribromo-4'-aminodiphenyl, m.p. 116° (Ac derivative, m.p. 220°), which gives 2:3:4-tribromodiphenyl, m.p. 225—227°, and 2:3:4:4'-tetrabromodiphenyl, m.p. 127°, also obtained from 3:4-dibromo-2:4'-diaminodiphenyl. The structures of (I) and (III) and their derivatives are confirmed by the above reactions, and by the fact that (I) does not react with piperidine (thus excluding the 3:4-dibromo-2-nitro-4'-aminodiphenyl structure).

E. W. W.

Diphenyl series. B. LONGO (Atti V Congr. Naz. Chim., 1936, 1, 386—388).—3-Nitro-*o*-toluidine diazotised and decomposed gives, not the nitroresol, but 7-nitroindazole. 6:6'-Diamino-2:2'-dimethyldiphenyl similarly treated yields a small amount of 2:2'-dimethyldiphenylene 6:6'-oxide. Prep. of 5:2'-dinitro-2-methyldiphenyl [from 2-iodo-4-nitrotoluene and o - $C_6H_4I \cdot NO_2$ (Cu), from which only 2:2'-dinitrodiphenyl is isolated] and of 2'-nitro-2:5-dimethyldiphenyl is attempted.

E. W. W.

Action of concentrated hydrochloric acid on arylazocarboxylamides [arylazoforamides]. R. JUSTONI (Atti V Congr. Naz. Chim., 1936, 1, 370—382).—This reaction gives semicarbazides chlorinated in the nucleus. Benzeneazocarboxylamide with conc. HCl at -15° forms *p*-chlorophenylsemicarbazide. This is converted by HNO_2 into *p*-chlorobenzeneazocarboxylamide, which when heated with conc. HCl gives 1:2':4'-dichlorophenylsemicarbazide (I), m.p. 192.5° (cf. *loc. cit.*) (synthesised from 2:4-dichlorophenylhydrazine and KCNO). This again gives 1:2':4'-dichlorobenzeneazocarboxylamide (II), m.p. 166—167° (decomp.) (from which it is re-formed by $SnCl_2$ reduction). 1-*o*-Chlorophenylsemicarbazide is oxidised ($KMnO_4$) to *o*-chlorobenzeneazocarboxylamide, which with HCl also gives (I). (II), also obtained from 2:4-dichlorobenzeneazocyanide, is converted by HCl into 1:2':4':6'-trichlorophenylsemicarbazide, m.p. 243—244°, which with HCl yields 2:4:6-trichlorobenzeneazocarboxylamide, m.p. 155° (decomp.). *p*-Tolueneazocarboxylamide forms 1-(3'-chloro-*p*-tolyl)semicarbazide (cf. *loc. cit.*), converted into 3-chloro-*p*-tolueneazocarboxylamide (III). Either of these with Br-KOH gives 3-chloro-*p*-tolylazoimide, which condenses with $CH_3Ac \cdot CO_2Et$ to form 1-(3'-chloro-*p*-tolyl)-5-methyl-1:2:3-triazole-4-carboxylic acid, m.p. 120°. With HCl, (III) gives 1-(3':5'-dichloro-*p*-tolyl)semicarbazide, m.p. 219—220°, reduced by $SnCl_2$ to 3:5-dichloro-*p*-toluidine, and oxidised by HNO_2 to 3:5-dichloro-*p*-tolueneazocarboxylamide. *p*-Nitrobenzeneazocarboxylamide and HCl yield 1-(2'-chloro-4'-nitrophenyl)semicarbazide, m.p. 219—

H (A, II.)

220°, converted by HNO_2 into 2-chloro-4-nitrobenzeneazocarboxylamide, m.p. 181.5° (decomp.).

E. W. W.

Action of halogen acids on arylazoforamidoximes [arylazocarboxylamidoximes]. A. QUILICO (Atti V Congr. Naz. Chim., 1936, 1, 514—522).—Benzeneazoforamidoxime and conc. HCl give the hydrochloride, m.p. 188° (decomp.), of *p*-chlorobenzeneazoforamidoxime, m.p. 209° (decomp.), which is again converted by conc. HCl into the hydrochloride, decomp. 190—194°, of 2:4-dichlorobenzeneazoforamidoxime, m.p. 172° (decomp.), from which the 2:4:6- Cl_3 -compound is obtained. Using HBr, the hydrobromide, m.p. 180° (decomp.), of *p*-bromobenzeneazoforamidoxime, m.p. 210° (decomp.), and the hydrobromide, m.p. 197—198° (decomp.), of 4-chloro-2-bromobenzeneazoforamidoxime, m.p. 185°, are obtained, together with 4-chloro-2:6-dibromo-, m.p. 206° (decomp.), and 2:4:6-tribromo-benzeneazoforamidoxime.

E. W. W.

Reaction of selenium dioxide with certain hydrazines. I. J. POSTOVSKI, B. P. LUGOVKIN, and G. F. MANDRIK (J. Gen. Chem. Russ., 1937, 7, 37—42).—Certain substituted hydrazines and SeO_2 react in aq. solution as follows: $NHR \cdot NH_2 \cdot HCl + SeO_2 \rightarrow R \cdot N_2Cl + Se + 2H_2O$ ($R = Ph$, *p*- C_6H_4Br , α - and β - $C_{10}H_7$, *m*- $C_6H_4 \cdot NO_2$). When $R = p$ - $C_6H_4 \cdot NO_2$, the reaction proceeds further: $R \cdot N_2Cl (I) \rightarrow R \cdot N_2 \cdot OH \rightarrow p$ - $NH_2 \cdot C_6H_4 \cdot NO_2$ (II) + HNO_2 ; (I) + (II) $\rightarrow NO_2 \cdot C_6H_4 \cdot NH \cdot N \cdot C_6H_4 \cdot NO_2$; $NHR \cdot NH_2 + HNO_2 \rightarrow NO_2 \cdot C_6H_4 \cdot N_3 + H_2O$. $NPh_2 \cdot NH_2$ is oxidised as follows: $NPh_2 \cdot NH_2 \rightarrow (NPh_2 \cdot NH)_2 \rightarrow NPh_2 + N_2$. Semicarbazide yields hydrazodicarbonamide. R. T.

Chloro- and bromo-nitrophenyl-hydrazines and -methylhydrazines and their derivatives. L. MAASKANT (Rec. trav. chim., 1937, 56, 211—232).— $NHMe \cdot NH_2$ and the appropriate halogenonitrobenzene in EtOH afford α -(4-nitrophenyl)-, α -(2-nitrophenyl)-, m.p. 63° (Ac derivative, m.p. 176°), α -(4-chloro-2-nitrophenyl)-, m.p. 91° (Ac derivative, m.p. 165°), α -(4-bromo-2-nitrophenyl)-, m.p. 93° (Ac derivative, m.p. 169°), α -methylhydrazine, which give the corresponding hydrazones of the following aldehydes (temp. are m.p.; — indicates no compound prepared): $PhCHO$, 137°, 85°, 150°, 149°; 2-, 198°, —, 132°, 133°, 3-, 154°, —, 153°, 131°, and 4-chloro-, 220°, 130°, 109°, 132°, 2-, —, —, 134°, 131°, 3-, —, 156°, 186°, 197°, and 4-nitro-, —, —, 182°, 171°, 4-methoxy-, 160°, 107°, 102°, 118°, 4-hydroxy-3-methoxy-, 189°, 147°, 120°, 150°, 2-hydroxy-, —, —, 140°, 128°, 3:4-methylenedioxy-, —, 136°, 129°, 144°, -benzaldehyde; furfuraldehyde, —, 130°, 134°, 143°, 5-methyl-, 120°, 61°, 105°, 93°, and hydroxymethyl-, 196°, 90°, 55—62°, 90°, -furfuraldehyde; $COPhMe$, 76°, —, —, —; $CH_3Ac \cdot CO_2Et$, 82°, —, —, —; *n*- $C_6H_{13}CHO$, 61°, —, —, —. N_2H_4 and 1:3:4- $C_6H_3Cl(NO_2)_2$ or $C_6H_3Br(NO_2)_2$ in EtOH afford 3-chloro-, 161° (Ac derivative, 190°), and 3-bromo-, 165° (Ac derivative, 211°), -6-nitrophenylhydrazine, which give the corresponding hydrazones of $PhCHO$, 175°, 190°, 2-, 186°, 211°, 3-, 235°, 235°, and 4-chloro-, 232°, 216°, 2-, 208°, 196°, 3-, 253°, 254°, and 4-nitro-, 275°, 263°, 2-, 230°, —, and 4-hydroxy-, 228°, 210—215°, 4-methoxy-, 187°, 210°, 3:4-methylenedioxy-, 218°, 210°, 4-hydroxy-3-

methoxy-, 210°, 207°, -benzaldehyde; cuminaldehyde, 168°, 167°; $\text{CH}_2\text{Ph}\cdot\text{CHO}$, 131°, 145°; CH_2O , 125°, 144°; MeCHO , 155°, 184°; $n\text{-C}_6\text{H}_{13}\cdot\text{CHO}$, 93°, 89°; COMe_2 , 130°, 138°; COEt_2 , —, 58°; COPh_2 , 160°, 152°; $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, 121°, 129°; furfuraldehyde, 198°, 204°; 5-methyl-, 194°, 164—172°, and hydroxymethyl-, 192°, 195°, -furfuraldehyde. J. D. R.

Mechanism of diazotisation. H. SCHMID [with G. MUHR] (Ber., 1937, 70, [B], 421—424).—The process of diazotisation in H_2SO_4 can be divided into a preliminary equilibration, $\text{NH}_3\text{Ph}' + \text{NO}_2' \rightleftharpoons \text{NH}_3\text{Ph}\cdot\text{NO}_2$ (I), and a time-decisive change, $(\text{I}) + \text{HNO}_2 \rightarrow \text{N}_2\text{Ph}' + \text{NO}_2' + 2\text{H}_2\text{O}$. Similar conditions are observed in HCl of low concn. but with increasing concn. of the latter the accelerating influence of Cl' becomes increasingly pronounced and ultimately is the controlling factor of the change. The component reactions are: $\text{NH}_3\text{Ph}' + \text{Cl}' \rightleftharpoons \text{NH}_3\text{PhCl}$ (II) and $(\text{II}) + \text{HNO}_2 \rightarrow \text{N}_2\text{Ph}' + \text{Cl}' + 2\text{H}_2\text{O}$. H. W.

Rapid determination of diazo-compounds. O. M. GOLESENKO (Zavod. Lab., 1936, 5, 598—600).—The entire diazo-N is rapidly eliminated as N_2 by shaking a solution of diazonium salt with $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$. The reaction is applied to the nitrometric determination of diazo-compounds. R. T.

Interaction of arylated unsaturated substances with diazonium salts. A. D. AINLEY and R. ROBINSON (J.C.S., 1937, 369—371).— p -Methoxystyrene and 2:4-dinitrobenzenediazonium sulphate (I), in EtOH afford anisaldehyde-2:4-dinitrophenylhydrazone, but similar treatment of styrene yields an unidentified substance, m.p. 76° (decomp.). With p -nitrobenzenediazonium chloride in EtOH, $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{CH}$ (II) yields p -methoxyphenylglyoxal- p -nitrophenylhydrazone, m.p. 261°, and $\text{CPh}:\text{CH}$, phenylglyoxyl- p -nitrophenylhydrazone, m.p. 252°. (I) and (II) in EtOH afford p -methoxyphenylglyoxal-2:4-dinitrophenylhydrazone (III), m.p. 235°, converted by 2:4- $\text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{NH}\cdot\text{NH}_2$ (IV) into p -methoxyphenylglyoxalbis-2:4-dinitrophenylhydrazone (V), m.p. 292°. (III) and (V) are also obtained from p -methoxyphenylglyoxal and (IV). J. D. R.

Manufacture of diazoamino-compounds.—See B., 1937, 216.

Condensation of methylene chloride with phenols. II. P. P. SCHORIGIN, I. P. LOSEV, and V. V. KORSCHAK (J. Appl. Chem. Russ., 1937, 10, 138—140).—Condensation of PhOH with CH_2Cl_2 takes place at 130° in presence of NH_3 , NH_2Me , NHMe_2 , or NMe_3 . R. T.

Reaction of metal chlorides with phenol and β -naphthol. H. FUNK and W. BAUMANN (Z. anorg. Chem., 1937, 231, 264—268; cf. A., 1928, 408).—The compound $\text{WCl}_2(\text{OPh})_4$, m.p. 136°, was prepared by refluxing WCl_6 with PhOH and CCl_4 . $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ gave the corresponding compound $\text{WCl}_2(\text{O}\cdot\text{C}_{10}\text{H}_7)_4$, m.p. 210°. Fusion of PhOH with WCl_6 gave the compound, $\text{W}(\text{OPh})_6$, m.p. 98°. The analogous compound, $\text{W}(\text{O}\cdot\text{C}_{10}\text{H}_7)_6$, m.p. 154°, is described. The compounds, $\text{Nb}(\text{OPh})_5$, m.p. 208°, and $\text{Ta}(\text{OPh})_5$, m.p. 224°, were prepared by adding the corresponding pentahalides to molten PhOH. The compounds, $\text{Nb}(\text{O}\cdot\text{C}_{10}\text{H}_7)_5$, m.p. 185°, and $\text{Ta}(\text{O}\cdot\text{C}_{10}\text{H}_7)_5$, m.p.

188° (decomp.), were prepared from the pentahalides and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ in presence of a solvent.

H. J. E.

Derivatives of o -[4-]*tert*-butyl-*m*-cresol. Preparation of musc ambrette. A. E. TSOHTSOHT-BABIN [with A. BESTOUGEY] (Bull. Soc. chim., 1937, [v], 4, 439—448).—2:6-Dinitro-4-*tert*-butyl-*m*-cresol (I), m.p. 97—98°, is best obtained by nitration in AcOH or Et_2O , but some mononitration, replacement and hydrolysis of the Bu, and formation of the quinone occurs even in these solvents; 2-, an oil, and 6-nitro-*tert*-butyl-, m.p. 163—165°, and 2:4:6-trinitro-*m*-cresol are thus obtained as by-products. (I) and $\text{Me}_2\text{SO}_4\text{-KOH}$ give musc ambrette (II). 4-*tert*-Butyl-*m*-tolyl acetate, b.p. 133—135°/16 mm., is unchanged by 90% HNO_3 in AcOH, but in Ac_2O gives a mixture of oily and solid (m.p. 165°) NO_2 -derivatives. The Me ether of (I) and $\text{Cu}(\text{NO}_3)_2$ in Ac_2O give mainly the 6- NO_2 -derivative, m.p. 59°, with 5—10% of the oily 2- NO_2 -compound and some 4-nitro-*m*-cresol, m.p. 55°. R. S. C.

Acyl derivatives of o -aminophenol. C. E. SPARKS and R. E. NELSON (Proc. Indiana Acad. Sci., 1934, 44, 132—134).—Condensation of o -hydrocinnamoylaminophenol with ClCO_2Me and of Me o -hydroxycarbanilate (I) with hydrocinnamoyl chloride affords the same *diacyl compound*, m.p. 60.8—61.5°. Similarly, o -isovalerylaminophenol and ClCO_2Me , and (I) and isovaleryl chloride, afford the same *diacyl compound*, m.p. 68—69°. CH. ABS. (r)

Behaviour of p -anisidine in binary systems containing phenols. K. HRYNAKOWSKI, H. STASZEWSKI, and B. SZULO (Rocz. Chem., 1937, 17, 20—29).—1:1 *Compounds* are formed in the systems p -anisidine (I)-PhOH (m.p. 58.4°), $-\alpha$ - (m.p. 58.5°) and $-\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ (m.p. 94°), and $-\text{m-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (transition point 52.6°), whilst compound formation does not take place in the systems (I)- o - and $-\text{p-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ and $-\text{p-toluidine}$ (II). The systems closely resemble the analogous ones with (II) in place of (I). The activity of the NH_2 -group is greater with OMe in the C_6H_6 ring than with Me. R. T.

Nitroamines. VII. Phenetylnitroamines. E. MACCIOTTA and (SIGNA.) V. DEFFENU (Atti V Congr. Naz. Chim., 1936, 1, 389—394).— $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ in $\text{KOEt-EtOH-Et}_2\text{O}$ is readily converted by EtNO_3 into the *K* salt of *p*-phenetylnitroamine (I), m.p. 54—55° (decomp.), which with Me_2SO_4 gives *p*-phenetylmethylnitroamine, m.p. 42—43°. The last rearranges in boiling aq. NaOH or in cold conc. H_2SO_4 to form 3-nitro-*p*-phenetidine, m.p. 109—110° (*Ac* derivative, m.p. 102—103°). As a by-product with (I), *pp*-diethoxyazobenzene, m.p. 157—158°, is obtained. The *K* salt of *o*-phenetylnitroamine (decomp. in air at room temp.) and *o*-phenetylmethylnitroamine, m.p. 50—51°, are obtained similarly, but less readily. Treatment of the nitroamine, in AcOH, with H_2SO_4 gives 5-nitro-*o*-phenetidine. The *K* salt of *m*-phenetylnitroamine is formed only extremely slowly and in poor yield. E. W. W.

Variations in taste of [acetyl derivatives of] dulcin. C. ALBERTI (Atti V Congr. Naz. Chim., 1936, 1, 271—279).—Dulcin yields, through its

$MgBr$ and $(MgBr)_2$ derivatives, Ac and Ac_2 derivatives, viz., N' -acetyl-, m.p. 220° , and NN' -diacetyl- N - p -phenethylcarbamide, m.p. 120° . These are both tasteless; their hydrolysis is studied. E. W. W.

Hydroxy-derivatives of 3:4-benzpyrene and 1:2-benzanthracene. L. F. FIESER, E. B. HERSEBERG, L. LONG, jun., and M. S. NEWMAN (J. Amer. Chem. Soc., 1937, 59, 475—478).—4'-Hydroxy-3:4-benzpyrene (I) [previously described (A., 1935, 1233) as 4'-hydroxy-1:2-benzpyrene] (acetate, m.p. 194 — 195° ; benzoate, m.p. 191 — 192° ; Me ether, m.p. 183 — 184° ; CO_2Me derivative, m.p. 243 — 244° ; p -nitrobenzoate, m.p. 252 — 253° ; p -aminobenzoate, m.p. 268 — 269°) is best obtained from 4'-keto-1':2':3':4'-tetrahydrobenzpyrene (modified prep.; cf. *ibid.*, 741) and S at 210 — 215° . 3-Methoxy-1:2-benzanthracene (II) is best prepared by reduction of the 10-anthrone with activated Zn dust and N -NaOH + PhMe. 3-Hydroxy-1:2-benzanthracene (III) (benzoate, m.p. 174 — 174.5° ; stearate, m.p. 87 — 89° ; CO_2Me derivative, m.p. 216 — 217°) coupled with diazotised (using Pr^oNO and AcOH—conc. H_2SO_4) p -NHAc- C_6H_4 - NH_2 gives the 4- p -acetamidobenzeneazo-, m.p. 278 — 279° (uncorr.), hydrolysed (EtOH-KOH) to the 4- p -aminobenzeneazo-derivative, amorphous, m.p. 211 — 213° (uncorr.). (III), $NaHSO_3$, and dioxan-aq. NH_3 at 180 — 190° afford 3-amino-1:2-benzanthracene, m.p. 211.5 — 212.5° ; 3-methylamino-1:2-benzanthracene, m.p. 115.5 — 116.5° , is similarly prepared using NH_2Me . All m.p. are corr. unless stated otherwise. (II) and (III) have weak carcinogenic properties; (I) appears to be inactive. H. B.

Condensation products of phenols with Δ^8 -octadecenyl alcohol.—See B., 1937, 218.

Hydroxyarylaminoanthracene derivatives.—See B., 1937, 217.

Preparation of 3:4-methylenedioxytoluene from 3:4-dihydroxytoluene. J. V. ASCHKINAZI and M. S. RABINOVITSCH (J. Appl. Chem. Russ., 1937, 10, 131—137).—3:4-Methylenedioxytoluene is obtained in 71% yield from 1:3:4- $C_6H_3Me(OH)_2$, CH_2Cl_2 , and KOH in 30% aq. EtOH or MeOH (18 hr. at 100°), in presence of bronze catalyst. R. T.

Contact changes of safrole. Y. FUJITA (J. Chem. Soc. Japan, 1935, 56, 1205—1209).—On passing safrole and H_2O through a Cu tube containing active C at 450 — 500° , isosafrole, pyrocatechol, 4-propylpyrocatechol, cresol, ethylpyrocatechol methylene ether, and p -ethylphenol are formed.

CH. ABS. (r)

Rearrangement of o -aminodiphenyl ethers. V. K. C. ROBERTS and J. A. RHYS (J.C.S., 1937, 39—41; cf. A., 1935, 1491).—The rates of rearrangement of some 5-substituted 2':4'-dinitro-2-aminodiphenyl ethers, $NHX \cdot C_6H_3R \cdot O \cdot C_6H_3(NO_2)_2$ ($R = OMe$, Me, H, I, Cl; $X = H$, and in some cases also Ac and o - $NO_2 \cdot C_6H_4 \cdot CO$), to the isomeric 4-substituted diphenylamines are recorded and are analogous to those of the corresponding 4-substituted ethers (cf. A., 1935, 484). Rearrangement of the 5-substituted ethers, unlike that of the 4-substituted ethers, is not catalysed by the simple alcohols. The 5-Me ether, but not any of the others, is rapidly rearranged by

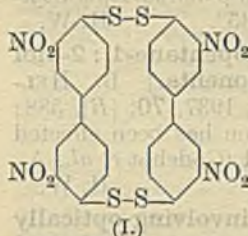
$C_5H_{11}N$, and the 5-OMe- and 5-Cl-ethers are stable towards all reagents tried. The following are described: 2':4'-dinitro-2-hydroxy-4-methoxydiphenylamine, m.p. 178° , exhibits chromoisomerism. 2':4'-Dinitro-2-hydroxy-5-methoxy-, m.p. 162° , -2-amino-5-methyl-, m.p. 134° (Ac, m.p. 146° , and o -nitrobenzoyl, m.p. 206° , derivative), and -2-amino-, m.p. 133° (cf. lit.), -diphenyl ether; 5-iodo-, m.p. 175° (o -nitrobenzoyl derivative, m.p. 194°), and 5-chloro-, m.p. 176° (o -nitrobenzoyl derivative, m.p. 202°), -2':4'-dinitro-2-aminodiphenyl ether; 2':4'-dinitro-2-hydroxy-4-methyl-, m.p. 166 — 167° (acetate, m.p. 145° ; o -nitrobenzoate, m.p. 185°), -2-hydroxy-, m.p. 205° (cf. lit.), -diphenylamine; 4-iodo-, m.p. 180° (o -nitrobenzoate, m.p. 206°), and 4-chloro-, m.p. 208° (two chromoisomeric forms; o -nitrobenzoate, m.p. 196°), -2':4'-dinitro-2-hydroxydiphenylamine. H. G. M.

Diphenyl series. IV. Preparation and properties of substituted diaminodiphenyls. H. H. HONGSON and P. F. HOLT (J.C.S., 1937, 37—38).—4:4'-Dichloro-3:3'-dinitrodiphenyl when refluxed with Na_2S_2 in EtOH- H_2O yields a polysulphide, m.p. $>340^\circ$ (decomposes suddenly if rapidly heated to this temp.), probably (I). This when reduced by Na-EtOH and then methylated (Me_2SO_4) yields 3:3'-dinitro-4:4'-dimethylthiol-diphenyl, m.p. 262° , reduced by Sn-HCl and by Fe-AcOH- H_2O to 3:3'-diamino-4:4'-dimethylthiol-diphenyl (II), m.p. 71° (dihydrochloride, m.p. 228° ; stannichloride, m.p. 242°), which when tetrazotised and then coupled with β - $C_{10}H_7$ -OH-NaOH gives 4:4'-dimethylthiol-diphenylene-3:3'-bisazo- β -naphthol, m.p. 318° . Similarly, reduction of 3:3'-dinitro-4:4'-dimethoxydiphenyl, m.p. 214° (obtained from the phenol and Me_2SO_4 - K_2CO_3 - H_2O), yields 3:3'-diamino-4:4'-dimethoxydiphenyl (III), m.p. 262° (dihydrochloride, m.p. 262° ; Ac_2 derivative, m.p. 330°), from which 4:4'-dimethoxydiphenylene-3:3'-bisazo- β -naphthol, m.p. 334° , was obtained. 4:4'-Dichloro-3:3'-, m.p. 133.5° , -2:3'-, m.p. 83° (Ac_2 derivative, m.p. 90°), and -2:2'-, m.p. 87° , -diaminodiphenyl were similarly prepared. (II) and (III) with Schaffer, H-, and J-acids give rise to a series of bisazo-dyes of much lower substantivity for cotton than that of the isomeric 3:3'-disubstituted 4:4'-bisazo-compounds. H. G. M.

Preparation of pure benzyl acetate. E. SHAPIRO (Maslob. Shir. Delo, 1935, 11, 321—322).—The prep. from $CH_2Ph \cdot OH$, Ac_2O , and H_3PO_4 is described.

CH. ABS. (r)

Acyl migrations. III. Use of ψ -nitrosites of phenolic ethers containing the propenyl group in the synthesis of α -arylated β -hydroxylamino- and β -amino-propanols. A. KRÄMLI and V. BRUCKNER (J. pr. Chem., 1937, [ii], 148, 117—125; cf. A., 1935, 972).—Anethole- ψ -nitrosite, m.p. 126° (decomp.), obtained by the action of conc. $NaNO_2$ and 20% H_2SO_4 on anethole in Et_2O , is smoothly converted by Ac_2O containing a little H_3PO_4 (d 1.75) into β -nitro- α - p -anisyl- n -propyl acetate, b.p. $195^\circ/3$ mm. (slight decomp.), the constitution of which is established by



its transformation by 20% KOH-EtOH into β -nitro-anethole, m.p. 47°. Electrolytic reduction of (I) in HCl at a technical Pb cathode at 35–40° gives β -N-acetylhydroxylamino- α -anisylpropan- α -ol (II).

p -OMe·C₆H₄·CH(OH)·CHMe·NAc·OH, m.p. 144°, which strongly reduces hot Fehling's solution, is immediately sol. in dil. alkali, and gives an intense violet colour with FeCl₃. Cold N -HCl-MeOH causes acyl migration in (II) with production of β -hydroxylamino- α - p -anisyl- n -propyl acetate, p -OMe·C₆H₄·CH(OAc)·CHMe·NH·OH, stable as the hydrochloride (III), m.p. 145° (decomp.), which is re-converted into (II) by 10% Na₂CO₃. Migration is not instantaneous since the compound,

p -OMe·C₆H₄·CH(OH)·CHMe·N<C(=O)Ph, m.p. 148°

(also derived from β -hydroxylamino- α - p -anisylpropan- α -ol), is obtained when (III) is emulsified with PhCHO-H₂O and Na₂CO₃ is gradually added. Under conditions described previously (*loc. cit.*) (I) is electrolytically reduced to β -acetamido- α - p -anisylpropan- α -ol (IV), m.p. 141°, transformed by N -HCl in COMe₂ into β -amino- α - p -anisyl- n -propyl acetate hydrochloride (V), m.p. 188°. Migration in the reverse direction occurs when (V) is treated with N -Na₂CO₃. (IV) is hydrolysed by 2*N*-HCl at 100° to β -amino- α - p -anisylpropan- α -ol hydrochloride, m.p. 235°. H. W.

[Resolution of *trans*-cyclopentane-1:2-diol into optically active components.] B. HELFERICH and R. HILTMANN (Ber., 1937, 70, [B], 588; cf. this vol., 146).—The resolution has been effected previously by a different method (Godchot *et al.*, A., 1935, 851). H. W.

Molecular rearrangements involving optically active radicals. VI. Displacement of hydroxyl by chlorine in optically active β -phenyl- β -methyl- n -butyl alcohol. E. S. WALLIS and P. I. BOWMAN (J. Org. Chem., 1936, 1, 383–392).—Resolution by means of quinine of α -phenyl- α -methylbutyric acid, prepared from β -methoxy- β -phenylbutane, b.p. 63–65°/2–3 mm. (obtained from the alcohol), gives the *l*-acid, $[\alpha]_D^{20} = -23.28^\circ$, the *l*-amide, m.p. 64–64.6°, $[\alpha]_D^{20} = -14.90^\circ$, of which is reduced to *l*- β -phenyl- β -methyl- n -butyl alcohol (I), b.p. 123–125°/12–13 mm., $\alpha_{563} = -4.20^\circ$, $\alpha_{589} = -4.90^\circ$, $\alpha_{546} = -5.78^\circ$, $\alpha_{486} = -7.35^\circ$, $\alpha_{435} = -9.6^\circ$ (pure liquid in 1-dm. tube at 19°) (*Bz* derivative, m.p. 46–46.2°). This with SOCl₂ gives 59.10% of CMeEt·CHPh (*NOCl* derivative, m.p. 105.7–106°), 31.3% of β -chloro- α -phenyl- β -methylbutane (II), and some of the corresponding carbinol formed by hydrolysis of the preceding chloride during purification of the reaction product. (II) had $[\alpha]_D^{20} = +0.63^\circ$ and the carbinol formed on hydrolysis had $[\alpha]_D^{20} = +0.88^\circ$ (pure liquid in 1-dm. tube). The intramol. rearrangement occurring in the formation of (II) from (I) and SOCl₂ takes place with partial racemisation and inversion in sign; an interpretation in terms of modern electronic theories is given. In the study of configurative relationships of compounds, the formation of optically active products is not trustworthy evidence for the absence of a complete structural change. H. G. M.

Condensation of methyl hexyl ketone with phenylacetylene. N. M. MALENOK and I. V. SOLOGUB

(J. Gen. Chem. Russ., 1936, 6, 1904–1909).—CPh:CH and Me *n*-hexyl ketone (I) yield β -hydroxy- β -phenylacetylenyloctane (II), b.p. 158°/5 mm., by the Grignard reaction. (II) regenerates CPh:CH and (I) with boiling 15% KOH, and gives β -phenylacetylenyl- Δ^8 -octene (III), b.p. 141–142°/5 mm., with Ac₂O (at the b.p.; 8 hr.). (III) and AcO₂H at 0° yield β - γ -dihydroxy- β -phenylacetylenyloctane, m.p. 76°, and its β -O-Ac derivative, b.p. 187°/6 mm. R. T.

Formation of benzhydrol from benzophenone in Grignard's reaction. S. P. LAGEREV (J. Gen. Chem. Russ., 1936, 6, 1766–1768).—MgPr²Cl and CPh₂ in Et₂O yield CHPh₂·OH and diphenylisopropylcarbinol, b.p. 148°/7 mm. R. T.

Dehydration of $\alpha\alpha$ -diphenyl- β -*o*-tolylethylene glycol. R. ROGER and F. C. HARPER (Rec. trav. chim., 1937, 56, 202–207).—*o*-C₆H₄Me·CO·CN is hydrolysed by HCl in EtOH to Et *o*-tolylglyoxylate, b.p. 135°/13 mm., reduced by Al-Hg in Et₂O to Et *o*-tolylglycollate, b.p. 140°/13 mm., which with MgPhBr affords $\alpha\alpha$ -diphenyl- β -*o*-tolylethylene glycol, m.p. 125–126°, dehydrated by conc. H₂SO₄ or AcOH to *o*-C₆H₄Me·CO·CHPh₂ and by 25% H₂SO₄ or fused H₂C₂O₄ to *o*-C₆H₄Me·CPh₂·CHO. J. D. R.

Oxidation of 3-epidihydrocholesterol acetate with chromic oxide. 3-epiHydroxyallocholanolic acid. S. KUWATA and T. TOYAMA (J. Pharm. Soc. Japan, 1935, 55, 978–984).—The oxidation affords 3-epiacetoxyallocholanolic acid (I), m.p. 199.5° (*Me* ester, m.p. 148°). The Na salt of (I), with EtOH-KOH, yields 3-epihydroxyallocholanolic acid, m.p. 244° (*Me* ether, m.p. 164.5°). (I) is oxidised to 3-ketoallocholanolic acid, m.p. 187°, with CrO₃. CH. ABS. (r)

Sterol group. XXIX. Constitution of the isomeric ethers of cholesterol. J. H. BEYNON, I. M. HEILBRON, and F. S. SPRING. XXX. Oxidation of ergosterol, ergosteryl and lumisteryl acetate with chromic anhydride. A. BURAWOY. XXXI. Structure of lumisterol. I. M. HEILBRON, G. L. MOFFET, and F. S. SPRING (J.C.S., 1937, 406–409, 409–411, 411–414; cf. A., 1936, 1105).—XXIX. The isomeric cholesterol ethers have *cis-trans* relationship and are correctly named *cis*- and *trans*-3-alkoxy- Δ^5 -cholestenes. "*cis*"-Cholesterol *Me* ether (I) with H₂-PtO₂ in AcOH at 65–70° gives cholestane and with conc. HNO₃ in AcOH at 0° gives 6-nitrocholesteryl nitrate, and the "*trans*"-*Me* ether (II) affords 6-nitro-3-methoxy- Δ^5 -cholestene, m.p. 114°, which is reduced by Zn dust in hot AcOH to 3-methoxycholestan-6-one, m.p. 92°, $[\alpha]_D^{20} = -11.2^\circ$ in CHCl₃ (*oxime*, m.p. 210°), and is also obtained from 6-ketocholestanol, MeI, and Ag₂O in C₆H₆. With Zn(OAc)₂ or KOAc in AcOH (I) gives quantitatively cholesteryl acetate, and with AcCl-C₅H₅N cholesteryl chloride, whereas (II) is unchanged. Br-KOAc converts (I) into tribromocholestane, wherefore this change is not due to HBr. *cis*-Cholestanol, "*mol.*" K (no reaction with Ag₂O), and MeI in C₆H₆ give by epimerisation *trans*-cholestanyl *Me* ether, m.p. 83°, $[\alpha]_D^{20} = +19.8^\circ$ in CHCl₃, which is unaffected by Br or HHal at room temp. The *cis*-ether could not be obtained.

XXX. Ergosterol (III) and lumisterol (IV) are

shown to have the conjugated ethylenic linkings at $C_{(5-6)}$ and $C_{(7-8)}$. CrO_3 and ergosteryl acetate in AcOH at 50° give 20% of ergostadiene-3:6-dion-5-ol, hydrolysed to a mixture of acidic and neutral products. Ergosteryl acetate and CrO_3 at 80° give 3-acetoxy-ergostadien-6-on-5-ol (V) (25%), m.p. 264° (decomp.), $[\alpha]_D^{25} -4.7^\circ$ in $CHCl_3$ (absorption max. at 2515 Å., subsidiary at 3330; 1 active H; unchanged by Ac_2O), reduced by $Al(OPr^i)_3$ to ergostadiene-3:5:6-triol-II. Lumisteryl acetate and CrO_3 at 45° give 3-acetoxy-lumistadien-6-on-5-ol, m.p. $177-178^\circ$, $[\alpha]_D^{25} +11.7^\circ$ in $CHCl_3$ [absorption very similar to that of (V)], also obtained from lumistadiene-3:5:6-triol monoacetate and CrO_3 at room temp.

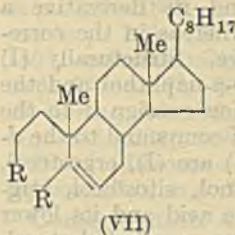
XXXI. Lumisteryl acetate gives a maleic anhydride adduct, m.p. $176-177^\circ$, $[\alpha]_D^{25} +28.2^\circ$ in $CHCl_3$, unchanged by distillation at $180^\circ/3 \times 10^{-4}$ mm., but quantitatively dissociated at $240^\circ/15$ mm. This acetate and H_2-PtO_2 in AcOH at $70-80^\circ$ give lumistenyl acetate, m.p. $178-179^\circ$, $[\alpha]_D^{25} -33.1^\circ$ in $CHCl_3$ (1 ethylenic linking proved by BzO_2H ; hydrolysed to lumistenol, m.p. $114-116^\circ$, $[\alpha]_D^{25} -0.5^\circ$ in $CHCl_3$), and lumistanol (VI), m.p. $126-127^\circ$. CrO_3 and (VI) give lumistanone, m.p. $121-122^\circ$, $[\alpha]_D^{25} -17.5^\circ$ in $CHCl_3$ (oxime, m.p. $165-166^\circ$), and lumistanedicarboxylic acid, m.p. $208-210^\circ$, $[\alpha]_D^{25} +24.6^\circ$ in $CHCl_3$ (Me_2 ester, m.p. $48-49^\circ$). $p-C_6H_4MeSO_2Cl$ converts (IV) into lumistatetraene, m.p. 88° , obtained also by $POCl_3$ (cf. ergosterol). Lumistadiene-3:5:6-triol-I and -II differ only in the orientation at $C_{(6)}$, since with CrO_3 both give lumistadiene-3:6-dion-5-ol, m.p. $182-183^\circ$. When distilled with Cu-bronze at $5-6$ mm., (IV) gives a ketone, $C_{28}H_{42}O$, m.p. $156-157^\circ$, $[\alpha]_D^{25} +5.5^\circ$ in $CHCl_3$ (2:4-dinitrophenylhydrazones, m.p. $204-205^\circ$; oxime, m.p. $168-169^\circ$), but dihydrolumisterol gives a lumistadienone, m.p. $175-176^\circ$, $[\alpha]_D^{25} +31.6^\circ$ in $CHCl_3$ [oxime, m.p. $210-212^\circ$ (decomp.)]. The above reactions and absorption spectra show that (III) and (IV) differ only stereochemically, in the orientation at $C_{(10)}$ and/or $C_{(14)}$ and possibly at $C_{(3)}$ and $C_{(9)}$. R. S. C.

Action of selenium dioxide on sterols and bile acids. III. Cholesterol. O. ROSENHEIM and W. W. STARLING (J.C.S., 1937, 377-384).—Cholesterol with SeO_2 in aq. AcOH affords cis- $\Delta^{5,6}$ -cholestene-3:4-diol (I), b.p. $255-260^\circ/0.2$ mm., m.p. $176-177^\circ$, $[\alpha]_D^{25} -60.0^\circ$ in $CHCl_3$, of which the following derivatives are described: diacetate (II), m.p. $169-170^\circ$, $[\alpha]_D^{25} -96.1^\circ$ in $CHCl_3$; 3-benzoate, m.p. $209-210^\circ$, $[\alpha]_D^{25} -30.7^\circ$ in $CHCl_3$ [from cholesteryl benzoate and SeO_2 in AcOH, or from (I) and $BzCl$ in C_5H_5N]; 3-benzoate 4-acetate, m.p. $166-167^\circ$, $[\alpha]_D^{25} -55.9^\circ$ in $CHCl_3$; dibenzoate, m.p. $150-151^\circ$, $[\alpha]_D^{25} -53.9^\circ$ in $CHCl_3$; bis-3:5-dinitrobenzoate, m.p. $220-221^\circ$, $[\alpha]_D^{25} -39.6^\circ$ in $CHCl_3$. (I) is oxidised (BzO_2H) to cis-cholestane-3:4-diol oxide, m.p. $173-174^\circ$, $[\alpha]_D^{25} +3.9^\circ$ in $CHCl_3$ (diacetate, m.p. $178-179^\circ$, $[\alpha]_D^{25} -22.1^\circ$ in $CHCl_3$), and with Br in $CHCl_3$ affords cis-cholestene-3:4-diol dibromide, m.p. $110-112^\circ$ (decomp.), which, when warmed in $COMe_2$, is converted into isopropylidenecholestene-3:4-diol, m.p. $133-134^\circ$, $[\alpha]_D^{25} -38.2^\circ$ in $CHCl_3$, also obtained from (I) in $COMe_2-HCl$. (I) is reduced (PtO_2-H_2) in AcOH to cis-cholestane-3:4-diol (III), m.p. $202-203^\circ$, $[\alpha]_D^{25} +18.8^\circ$ in $CHCl_3$

(diacetate, m.p. $136-137^\circ$, $[\alpha]_D^{25} -7.1^\circ$ in $CHCl_3$), cholestane (IV), and cholestane-3-ol (V). With Pd-C, (I) is reduced in EtOH to (IV), (V), and coprostanol (VI), whilst (II) in AcOH or neutral solution affords (IV) and (V). (I) is oxidised by $Pb(OAc)_4$ in AcOH to the dialdehyde (VII); R = CHO (di-o-tolylsemicarbazone, m.p. $192-193^\circ$; disemicarbazone, m.p. $218-219^\circ$), which is oxidised (H_2O_2 -AcOH) to Diels' acid (VII; R = CO_2H), also obtained by oxidation of (I) with $KOBr$. Oxidation [$Pb(OAc)_4$] of (III) affords dihydro-Diels' acid. With HCl in EtOH, or with H_2O at 200° , (I) affords coprostenone (cholestenone) (VIII) (o-tolylsemicarbazone, m.p. $243-244^\circ$; 2:4-dinitrophenylhydrazones, m.p. $233-234^\circ$). Cholesteryl acetate, oxidised [$Pb(OAc)_4$] followed by acetylation and hydrolysis of the product, yields trans- $\Delta^{5,6}$ -cholestene-3:4-diol (IX), m.p. $257-258^\circ$, b.p. $255-260^\circ/0.2$ mm., $[\alpha]_D^{25} +6.0^\circ$ in C_6H_5N , of which the following derivatives are described: diacetate (X), m.p. $135-136^\circ$, $[\alpha]_D^{25} -13.3^\circ$ in $CHCl_3$; dibenzoate, m.p. $181-182^\circ$, $[\alpha]_D^{25} -74.4^\circ$ in $CHCl_3$; 3-benzoate 4-acetate, m.p. $128-129^\circ$, $[\alpha]_D^{25} -21.2^\circ$ in $CHCl_3$; dibromide, m.p. $196-197^\circ$. (IX) is oxidised by BzO_2H to trans-cholestane-3:4-diol oxide, m.p. $164-165^\circ$, $[\alpha]_D^{25} -7.5^\circ$ (diacetate, m.p. $154-155^\circ$, $[\alpha]_D^{25} -58.5^\circ$). (X) is reduced (PtO_2-H_2 in Et_2O -AcOH) to (IV), (V), and trans-cholestane-3:4-diol, m.p. $194-195^\circ$, $[\alpha]_D^{25} +10.2^\circ$ (diacetate, m.p. $140-141^\circ$); reduction with Pd catalysts yields (IV), (V), and (VI). (IX) with HCl-EtOH affords (VIII) and a substance, $C_{27}H_{46}O_2$, m.p. $139-140^\circ$. (IX) is also obtained by debromination of cholesterol dibromide with NaOAc. The ease of dehydration of (I) and (IX) to (VIII) is discussed in relation to the biochemical problem of the conversion of cholesterol into coprosterol in the animal organism. J. D. R.

Transformation of ergosterol with nickel. F. LAUCHT (Z. physiol. Chem., 1937, 246, 171-176; cf. Windaus, A., 1929, 1065).—Ergosterol heated with Ni at 225° for 3.5 hr. in absence of air and reduced with Na in EtOH gives a compound (I), m.p. 195° , $[\alpha]_D^{25} +13.9^\circ$ in $CHCl_3$, of dihydroergosterol (II) and u-ergostadienol (III), m.p. 170° , $[\alpha]_D^{25} +50.6^\circ$ in $CHCl_3$. When (I) in the min. amount of hot $CHCl_3-C_5H_5N$ is treated with $BzCl$ the benzoate of (II) separates. The more sol. benzoate of (III) is hydrolysed with KOH in EtOH and traces of (II) are removed with digitonin. The acetate of u-ergostanol (IV) with CrO_3 gives an oil, probably a hydroxyketone analogous to pregnanolone, which yields a semicarbazone, m.p. 232° . (IV) with CrO_3 in AcOH gives the corresponding ketone, m.p. 94° , which, in AcOH, with Zn + HCl gives u-ergostane, m.p. 55° , $[\alpha]_D^{25} +20^\circ$. (IV) combines with ergostanol and is probably homologous with epi-coprosterol. W. McC.

Stereochemistry of the sterols and related, natural substances. H. LETTRÉ (Ber., 1937, 70, [B], 450-452).—Examination of the optical activity of neoergosterol (I) and its derivatives shows the $[\alpha]_D$ is composed of a portion B determined by the asym-



metric centre $C_{(3)}$ and a part A dependent on the other asymmetric centres. In (I) and its derivative a negative val. is assigned to B whereas in the corresponding *epi*-series it is positive. Structurally (I) appears related to *ac*-tetrahydro- β -naphthol and the observed displacements of rotation consign it to the *l*-isomeride (II) and hence the *epi*-compound to the *d*-substance (III). Related to (II) are (I), ergosterol, cholesterol, ergosterol, cholestanol, sitosterol, stigmasterol, β -3-hydroxyallocholanolic acid and its lower homologues, *trans*-androsterone, *allo*cholesterol, coprosterol, β -3-hydroxycholanolic acid and its lower homologues, tigogenin, and uzarigenin with OH at $C_{(3)}$ *cis* to Me at $C_{(10)}$. (III) is related to *epineo*ergosterol, *epi*cholesterol, *epi*ergosterol, *epi*cholestanol, β -3-hydroxyallocholanolic acid and its lower homologues, androsterone, *epiallo*cholesterol, *epi*coprosterol, lithocholic acid and its lower homologues, and digitoxigenin with OH at $C_{(3)}$ *trans* to Me at $C_{(10)}$. H. W.

Provitamin-D activity and structure. Addition of Grignard reagents to 7-ketocholesteryl acetate. S. WEINHOUSE and M. S. KHARASCH (J. Org. Chem., 1936, 1, 490—495).—7-Ketocholesteryl acetate (I) and $MgMeI$ in C_6H_6 give 7-hydroxy-7-methylcholesterol, m.p. 164—165° (*Bz* derivative, m.p. 172—173°), and 7-methylencholesterol, m.p. 81—82° (*Bz* derivative, m.p. 139—140°); $MgEtBr$ yields only 7-ethylidenecholesterol, m.p. 66—68° (*Bz* derivative, m.p. 109—110°). $MgBu^sBr$ gives 7-isobutylidenecholesterol, m.p. 120—121° (from the *Bz* derivative, m.p. 164—165°); the crude product heated at 200° or slowly distilled at low pressure, and irradiated, is antirachitic. Only side-chain dehydration (as indicated by absorption spectra) of 7-OH-compounds is observed; 7-hydroxy-7-phenylcholesterol, m.p. 151—152° (*Bz* derivative, m.p. 201—202°), from $MgPhBr$, could not be dehydrated. 7-Ethylidenecholesteryl acetate, m.p. 110—111°, is oxidised (CrO_3 -AcOH) to (I). E. W. W.

Condensation of ethyl dichloroacetate with ketones and aldehydes by magnesium amalgam. G. DARZENS and A. LEVY (Compt. rend., 1937, 204, 272—274).—*cyclo*Hexanone condenses with $CHCl_2 \cdot CO_2Et$ in the presence of Mg amalgam (30°) to yield *Et* 1-hydroxycyclohexylchloroacetate, b.p. 130—140°/4 mm., dehydrated (P_2O_5) to *Et* cyclohexylidenechloroacetate, b.p. 138—139°/16 mm., which with $NaOH$ -aq. $EtOH$ affords α -ketocyclohexylacetic acid which in turn gives cyclohexylaldehyde. Similarly cyclopentanone affords *Et* 1-hydroxycyclopentylchloroacetate, b.p. 128°/15 mm., whilst $PhCHO$ yields *Et* α -chloro- β -hydroxyphenylpropionate, b.p. 165°/4 mm., which is dehydrated to $BzCO_2H$ and with $NaOEt$ gives *Et* α - β -epoxyphenylpropionate. With the appropriate aliphatic aldehydes *Et* α -chloro- β -hydroxybutyrate, b.p. 100—105°/15 mm., *nonoate*, b.p. 144—148°/5 mm., and γ -methyl-*n*-valerate, b.p. 112—115°/18 mm., are produced. F. N. W.

Diaryl-*p*-nitrobenzamidines. R. C. SHAH (J. Univ. Bombay, 1936, 5, Part II, 62—68).—*p*-Nitrobenzanilide (from p - $NO_2 \cdot C_6H_4 \cdot COCl$ and NH_2Ph in $NPhEt_2$), new m.p. 216°, gives the imidochloride (I), which with NH_2Ph in $NPhEt_2$ gives diphenyl-*p*-nitrobenzamidine, $+0.5C_6H_6$, CCl_4 , $EtOH$, $CHCl_3$, or

C_5H_5N , m.p. 155° [*hydrochloride*, m.p. 280—290° (decomp.); *sulphate*, m.p. 210—215° (decomp.)]; *Ac*, m.p. 155—156°, and *Bz* derivative, m.p. 152—153°, reduced by Zn - $AcOH$ or NH_4HS to the aminobenzamidine. *p*-Nitrobenz-*p*-toluidide, new m.p. 207—208°, with PCl_5 gives the imidochloride (II), m.p. 120° (cf. Gattermann *et al.*, A., 1892, 839), converted by NH_2Ph in $NPhEt_2$ into phenyl-*p*-tolyl-*p*-nitrobenzamidine, m.p. 138° [*hydrochloride*, m.p. 290—300° (decomp.); *sulphate*, m.p. 270—275° (decomp.)]; *Bz* derivative, m.p. 157—158°, also obtained from (I) and p - $C_6H_4Me \cdot NH_2$ in $NPhEt_2$. (II) and p - $C_6H_4Me \cdot NH_2$ afford di-*p*-tolyl-*p*-nitrobenzamidine, m.p. 160° (*hydrochloride*, m.p. >300°; *sulphate*, m.p. 198—201°; *Bz* derivative, m.p. 163—164°). R. S. C.

Condensation of aminomethylisopropylcarbinol (α -amino- γ -methylisobutyl alcohol) with benzaldehyde, cyclohexanone, and hydrocyanic acid, by Strecker's method. V. F. LIUBOMUDROV and S. V. TZUKERMAN (Ukrain. Chem. J., 1937, 12, 21—25).— $OH \cdot CHPr^s \cdot CH_2 \cdot NH_2 \cdot HCl$, KCN , and $PhCHO$ in aq. $EtOH$ (24 hr. at room temp.) yield phenyl- β -hydroxyisomethylaminoacetone, m.p. 63—64° (*hydrochloride*, m.p. 120—124°), hydrolysed by boiling with HCl to phenyl- β -hydroxyisomethylaminoacetic acid, m.p. 208—209° (*hydrochloride*, m.p. 164—165°). 1- β -Hydroxyisomethylaminohexahydro-benzonitrile, m.p. 59—60° (*hydrochloride*, m.p. 112—117°), and benzoic acid [*hydrochloride*, m.p. 234—238° (decomp.)] are obtained analogously, using cyclohexanone in place of $PhCHO$. R. T.

Synthesis of cyclohexanespirocyclopentane. R. D. DESAI and M. A. WALI (J. Univ. Bombay, 1936, 5, Part II, 69—72).— Et sodio-1-cyanocyclohexane-1-cyanoacetate and $CH_2I \cdot CH_2 \cdot CO_2Et$ give *Et* α -cyano- α -1-cyano-1-cyclohexylglutarate, b.p. 227—228°/15 mm., converted by H_2SO_4 followed by $EtOH$ - H_2SO_4 into *Et* α -1-carbethoxy-1-cyclohexylglutarate, b.p. 174—175°/15 mm., which with alkali gives α -1-carboxy-1-cyclohexylglutaric acid, m.p. 165—168° (decomp.). The Na_2 salt thereof with Ac_2O at 130—140°, followed by H_2SO_4 - $EtOH$, gives *Et* cyclohexanespirocyclopentan-2-one-5-carboxylate, b.p. 141—142°/15 mm., and thence the corresponding acid, m.p. 104—105°; Clemmensen reduction affords the crude cyclopentane acid, the Ca salt of which with soda-lime affords cyclohexanespirocyclopentane, b.p. 70—75°/15 mm. (tetrabromide, m.p. 131—132°). R. S. C.

Configurative relationships of the aliphatic and aromatic amino-acids. P. A. LEVENE and S. MARDASHEW (J. Biol. Chem., 1937, 117, 179—182).—Oxidation (CrO_3 - $AcOH$; water-bath; 3 hr.) of *N*-benzoyl-*l*-tyrosine *Et* ester, obtained from *l*-tyrosine, followed by hydrolysis with HCl , gives *l*-aspartic acid. H. G. M.

Configurative relationship of mandelic acid to lactic acid. M. KUNA and P. A. LEVENE (J. Biol. Chem., 1937, 118, 315—320).—The configurative relation of *l*-mandelic acid to *l*-lactic acid is established chemically (cf. A., 1936, 466). *l*-Acetylmandelic acid is hydrogenated (Adams; 3 atm.) to (+)-acetyl-cyclohexylglycollic acid (acetylhexahydromandelic acid), b.p. 115—120°/0.1 mm., $[\alpha]_D^{25} +17.7^\circ$, which is also obtained, b.p. 135—140°/0.3 mm., $[\alpha]_D^{25} +11.1^\circ$, by

KMnO₄-COMe₂ oxidation of (+)- α -cyclohexylcrotyl acetate, b.p. 87°/1 mm., [α]_D²⁵ +6.51°, the acetylation (C₆H₅N) product of (–)-propenylcyclohexylcarbinol, b.p. 108–109°/15 mm., [α]_D²⁰ –10.4°. The last is obtained by resolving the product from Mg cyclohexyl bromide and CHMe·CH·CHO through the brucine salt of the *H* phthalate, and is correlated, by hydrogenation (Adams), to *l*-cyclohexyl-*n*-propylcarbinol (A., 1932, 1027), which has already been related to *l*-lactic acid, through (–)-phenyl-*n*-propylcarbinol, (+)-*n*-propyl-*n*-hexylcarbinol, and (–)- α -hydroxyoctoic acid.

E. W. W.

Isomeric menthyl *o*-nitromandelates. E. B. ABBOT, A. MCKENZIE, and P. A. STEWART (Ber., 1937, 70, [B], 456–462).—Esterification of *r*-*o*-nitromandelic acid (I) by *l*-menthol and HCl at 100° gives a non-homogeneous product from which (–)-menthyl (+)-*o*-nitromandelate (II), m.p. 83–85°, [α]_D²⁰₅₈₉₃ +152.7°, [α]_D²⁰₅₇₉₁ +161.9°, [α]_D²⁰₅₄₀₁ +201.5° in COMe₂, [α]_D²⁰₅₈₉₃ +172.7°, [α]_D²⁰₅₇₉₁ +184.1°, [α]_D²⁰₅₄₀₁ +227.2° in EtOH, is isolated by repeated crystallisation from EtOH. (–)-Menthyl (–)-*o*-nitromandelate (III), obtained by esterification of the acid, has m.p. 66°, [α]_D^{20.5}₅₈₉₃ –320°, [α]_D^{20.5}₅₇₉₁ –339°, [α]_D^{20.5}₅₄₆₁ –407° in COMe₂, [α]_D²⁰₅₈₉₃ –336.5°, [α]_D²⁰₅₇₉₁ –355.9°, [α]_D²⁰₅₄₆₁ –427.3° in EtOH. Admixture of equal amounts of (II) and (III) affords (–)-menthyl *dl*-*o*-nitromandelate (IV), m.p. 65–67°, [α]_D²⁰₅₈₉₃ –81° in EtOH, which could not be crystallised unchanged. Esterification of (–)-*o*-nitromandelic acid with *dl*-menthol (V) yields a product separated into (+)-menthyl (–)-*o*-nitromandelate (VI), m.p. 83–85°, [α]_D^{20.5}₅₈₉₃ –153.4°, [α]_D^{20.5}₅₄₀₁ –201.8° in COMe₂, and (III). Hydrolysis of (VI) yields (+)-menthol, m.p. 41–42°, [α]_D¹⁴₅₈₉₃ +50°. (+)-Menthyl (+)-*o*-nitromandelate (VII), obtained by esterification, has m.p. 66° [α]_D²⁰₅₈₉₃ +319°, [α]_D²⁰₅₇₉₁ +339°, [α]_D²⁰₅₄₆₁ +407° in COMe₂. (IV) undergoes asymmetric catalytic racemisation in presence of KOH–EtOH. The product of the esterification of (I) by (V) in presence of HCl is separated by crystallisation into the α -ester (VIII), rhombic plates, m.p. 88–89°, also obtained by admixture of equal amounts of (III) and (VII), and the β -ester (IX), m.p. 74–75°. Admixture of equal amounts of (II) and (VI) gives a non-homogeneous product from which the γ -ester (X), needles, m.p. 90°, is derived. Equal quantities of (VIII) and (X) readily give (IX). At >75° the products of the interaction of (I) and PCl₅ explode.

H. W.

Modifications in the spectra of aqueous solutions of phenylpyruvic acid as a function of p_{H} and time.—See A., I, 236.

Derivatives of 1-hydroxy-2-naphthoic acid.
III. Arylamides and their bromination products. G. V. JADHAV, S. N. RAO, and N. W. HIRWE (J. Univ. Bombay, 1936, 5, Part II, 137–141; cf. this vol., 149).—Anilides, toluidides, and anisidides of 1:2-OH·C₁₀H₆·CO₂H are brominated first in the 4-position of the C₁₀H₆ and then in the Ph. Structures are proved by synthesis from the Br-acid and/or Br-amine. The following are described: 1-hydroxy-2-naphth-anilide, new m.p. 155–156°, -*m*-, m.p. 118–119°, -*o*-, m.p. 89–90°, and -*p*-toluidide, m.p. 148–149°, -*o*-, m.p. 161–162°, and -*p*-anisidide, m.p. 129–130°, -*o*-, m.p. 141–142°, and -*p*-phenetidide,

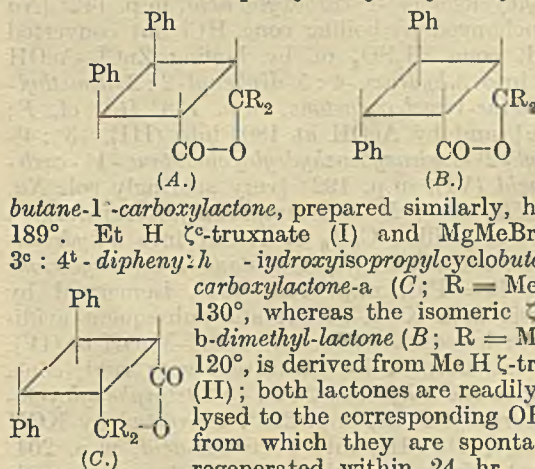
m.p. 154–155°; 4-bromo-1-hydroxy-2-naphth-*o*-, m.p. 180–181°, and -*p*-anisidide, m.p. 155–156°, -*o*-, m.p. 190–191°, and -*p*-phenetidide, m.p. 179–180°, -*p*-bromoanilide, m.p. 197–198°, -5'-bromo-*o*-, m.p. 177–178°, -4'-bromo-*m*-, m.p. 171–172°, and -2'-bromo-*p*-toluidide, m.p. 213–214°, -??-dibromo-*o*-, m.p. 233–234°, and 4'-bromo-*p*-anisidide, m.p. 196–197°, -??-dibromo-*o*-, m.p. 227–228°, and -4'-bromo-*p*-phenetidide, m.p. 201–202°.

R. S. C.

Configuration of the diphenylcyclobutanone-carboxylic acids. XXI. R. STOERMER and H. STARCK (Ber., 1937, 70, [B], 479–482).—Successive treatments of the 3-isopropylidene-2:4-diphenylcyclobutane-1-carboxylic acid (I) (*Me* ester, m.p. 108–109°) derived from γ -truxillic acid (A., 1936, 71) with morphine and brucine in MeOH give with some uncertainty the corresponding (+)-acid (II), m.p. 144–145°, [α]_D +67.5° in EtOH [(?) hydrated morphine salt, m.p. 117–118°], and (–)-acid (III), m.p. 143–144°, [α]_D –62.75° in EtOH (brucine salt; *Me* ester, m.p. 86–87°). (II) has therefore the constitution *A* (R = CMe₂). Ozonisation of (II) in EtOAc yields (–)-2:4-diphenylcyclobutan-3-one-1-carboxylic acid (IV), m.p. 143–144°, [α]_D –33.4° in AcOH, whilst the corresponding (+)-acid (V), m.p. 143–144°, [α]_D +37.4° in AcOH, is derived similarly from (III). The *r*-acid (*loc. cit.*) has therefore the structure *A* (R = O). Treatment of (IV) or (V) with hot aq. media, AcOH, or EtOH gives the isomeric diphenylcyclobutanonecarboxylic acid, m.p. 98° (*loc. cit.*), the *Me* ester, m.p. 72°, of which results when either acid is subjected to CH₂N₂.

H. W.

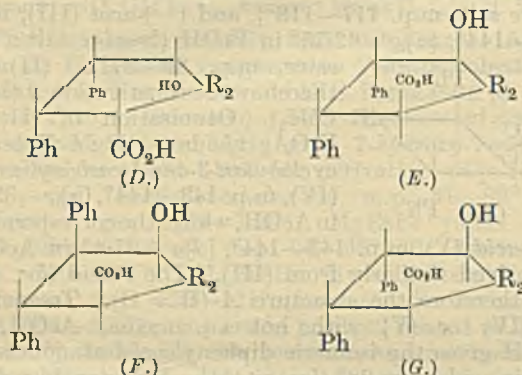
Ring enlargement in the truxinic acid series. XXII. R. STOERMER, G. STARCK, and H. E. ANKER (Ber., 1937, 70, [B], 483–498).—Et H β -truxinate is converted by MgMeBr in Et₂O into 3':4'-diphenyl-2'-hydroxyisopropylcyclobutane-1'-carboxylactone (*A*; R = Me), m.p. 120–121°, which could not be converted into the corresponding OH-acid, isomerised by heating with acid or alkali, or converted into the anilide or amide by heating with NH₂Ph or NH₃ at 250°. 3':4'-Diphenyl-2'-hydroxybenzhydrylcyclo-



butane-1'-carboxylactone, prepared similarly, has m.p. 189°. Et H ζ -truxinate (I) and MgMeBr afford 3':4'-diphenyl-2'-hydroxyisopropylcyclobutane-1'-carboxylactone-*a* (*C*; R = Me), m.p. 130°, whereas the isomeric ζ -truxin-*b*-dimethyl-lactone (*B*; R = Me), m.p. 120°, is derived from Me H ζ -truxinate (II); both lactones are readily hydrolysed to the corresponding OH-acids, from which they are spontaneously regenerated within 24 hr. (I) and MgPhBr give the expected moderately stable OH-acid

(Na salt) converted by boiling Ac_2O into 3':4'-diphenyl-2'-hydroxybenzhydrylcyclobutane-1'-carboxylactone (C; R = Ph), m.p. 222°. Similarly (II) yields the expected OH-acid which is too unstable to permit recrystallisation and readily passes into ζ -truxin-b-diphenyl-lactone (B; R = Ph), m.p. 164°.

The following examples of ring enlargement are cited. The products are very resistant towards oxidation and, under drastic conditions, give only BzOH and COPh_2 which have no diagnostic val. The configurations are based on analogy with the behaviour of the truxinic acids towards isomerising agents and on the experience of the corresponding ring contraction. Et H neotruxinatate b and MgMeBr give 3':4'-diphenyl-2'-hydroxyisopropylcyclobutane-1'-carboxylic acid, m.p. 165–167°, converted by P_2O_5 in boiling AcOH into 3-hydroxy-4:5-diphenyl-2-gemdimethylcyclopentane-1-carboxylactone (III) (cf. D; R = Me),



m.p. 146°; similarly MgPhBr yields 3':4'-diphenyl-2'-hydroxybenzhydrylcyclobutane-1'-carboxylic acid, m.p. 210° (very sparingly sol. Na salt; Me ester, m.p. 170°), whence 3-hydroxy-2:2:4:5-tetraphenylcyclopentane-1-carboxylactone (IV) (cf. D; R = Ph), m.p. 131–132°. Et H neotruxinatate a affords 3':4'-diphenyl-2'-hydroxybenzhydrylcyclobutane-1'-carboxylic acid, m.p. 222–223° (NH_4 salt; Me ester, m.p. 165°), whence the 3-hydroxy-2:2:4:5-tetraphenylcyclopentane-1-carboxylactone (V) (cf. E; R = Ph), m.p. 163–164°. Me H δ -truxinate, m.p. 109–110° (Na and Ca salts), gives 3':4'-diphenyl-2'-hydroxyisopropylcyclobutane-1'-carboxylic acid, m.p. 142° (Na salt), unchanged by boiling conc. HCl but converted by cold, conc. H_2SO_4 or by boiling ZnCl_2 - AcOH mainly into 3-hydroxy-4:5-diphenyl-2:2-dimethylcyclopentane-1-carboxylactone, m.p. 159° [(?) cf. F; R = Me], and by AcOH at 180° into (III). 3':4'-Diphenyl-2'-hydroxybenzhydrylcyclobutane-1'-carboxylic acid (VI), m.p. 192° (very sparingly sol. Na, K, and NH_4 salts; Me ester, m.p. 152°), is transformed by P_2O_5 in boiling C_6H_6 or AcOH into 3-hydroxy-2:2:4:5-tetraphenylcyclopentane-1-carboxylactone (cf. G; R = Ph), m.p. 163–164°, isomerised by hydrolysis with KOH - MeOH and subsequent acidification or by contact with cold KOH - MeOH to (IV). (VI) is transformed by trituration with cold, conc. H_2SO_4 into the 3-hydroxy-2:2:4:5-tetraphenylcyclopentanecarboxylactone, m.p. 228°, converted by KOH in boiling $(\text{CH}_3\text{OH})_2$ into a cis-OH-acid, m.p. 204° (decomp.) (Na salt), which passes into an isomeric lactone, m.p. 256°. These lactones are not isomerised

by $\text{KOH}-(\text{CH}_3\text{OH})_2$ whereas (IV) and (V) [probably with intermediate formation of (IV)] yield two transforms of 3-hydroxy-2:2:4:5-tetraphenylcyclopentane-1-carboxylic acid, m.p. 192° (Na, K, and NH_4 salts; Me ester, m.p. 152°) and m.p. 180–181° (NH_4 salt; Me ester, m.p. 123–124°), neither of which can be lactonised. During the prep. of (III), 3':4'-diphenyl-2'-isopropenylcyclobutane-1'-carboxylic acid, m.p. 141° (Na salt), is produced. Its constitution follows from its ozonisation to 2'-acetyl-3':4'-diphenylcyclobutane-1'-carboxylic acid, m.p. 167° (semicarbazone, m.p. 231°), which is degraded by NaOBr to neotruxinic acid. Similarly, 3':4'-diphenyl-2'-isopropenylcyclobutane-1'-carboxylic acid is ozonised to 2'-acetyl-3':4'-diphenylcyclobutane-1'-carboxylic acid, m.p. 145° [semicarbazone, m.p. 192° (decomp.)].

The following compounds are incidentally described: 3':4'-diphenyl-1':2'-dihydroxyisopropylcyclobutane, m.p. 230°; 3':4'-diphenyl-1':2'-dihydroxydiphenylmethylcyclobutane, m.p. 204°, converted by Ac_2O into an anhydride, $\text{C}_{42}\text{H}_{35}\text{O}$, m.p. 150°; 1':2'-dibenzoyl-3':4'-diphenylcyclobutane, m.p. 250°, which does not yield a semicarbazone. H. W.

Detection of quinic acid in presence of shikimic acid in the carpels of *Illicium verum*, Hook., and the preparation of quinic acid derivatives. A. BOLDT (Pharm. Zentr., 1937, 78, 157–166).—After removal of oil and protocathechuic acid from the solvent extract of the carpels of *I. verum*, quinic acid can be isolated from its mixture with shikimic acid in the residue and characterised by formation of triacetylquinide, m.p. 134–135°. Triacetylquinic acid, m.p. 188°, tribenzoylquinide, m.p. 151°, and quinide (prep. by heating quinic acid in $\text{C}_2\text{H}_5\text{Cl}$) are described.

E. H. S.

Alkyl methylphthalates. M. HAYASHI and S. TSURUOKA (J. Chem. Soc. Japan, 1935, 56, 999–1007).— Me_1 , m.p. 114.5–115°, and Et_1 , m.p. 86–87°, 3-methylphthalate are described. CH. ABS. (r)

Condensation of succinic anhydride with α - and β -naphthyl methyl esters. R. D. DESAI and M. A. WALI (J. Univ. Bombay, 1936, 5, Part II, 73–76).— $(\text{CH}_2\text{CO})_2\text{O}$, $\alpha\text{-C}_{10}\text{H}_7\text{OMe}$, and AlCl_3 in PhNO_2 give γ -keto- γ -4-methoxy-1-naphthylbutyric acid, m.p. 177–178° (reduced in poor yield to the known 1- $\text{C}_{10}\text{H}_7\text{[CH}_2\text{]}_3\text{CO}_2\text{H}$), but in CS_2 much (?) 4-methoxynaphthalenedithiocarboxylic acid, m.p. 225°, is also formed. $\beta\text{-C}_{10}\text{H}_7\text{OMe}$ in PhNO_2 gives mainly γ -keto- γ -6-methoxy-2-, m.p. 148° (cf. Fieser and Peters, A., 1933, 67) (oxidised to 6:2- $\text{O-Me-C}_{10}\text{H}_6\text{CO}_2\text{H}$), and some γ -keto- γ -2-methoxy-1-naphthylbutyric acid, m.p. 136–137°, the latter acid being the main product (with some thio-acid) in CS_2 . R. S. C.

Naphthalylmalonic and peri-naphthindandionecarboxylic esters. J. SUSZKO and M. WDOVICI (Bull. Acad. Polonaise, 1936, A, 293–298).— $\text{CHNa}(\text{CO}_2\text{Et})_2$ with 1:8- $\text{C}_{10}\text{H}_6(\text{COCl})_2$ in C_6H_6 affords Et_2 naphthalylmalonate (I), m.p. 143°, hydrolysed (boiling KOH) to the dicarboxylic acid, but with NH_3 in warm EtOH converted into naphthalimide, which indicates that (I) has an unsymmetrical structure. (I) with conc. H_2SO_4 affords CO_2 and Et peri-naphthindandionecarboxylate, m.p. 139–140°, which with boiling 5% KOH affords the acid, m.p. 268—

269° (decomp.), decarboxylated at 260°/20 mm. to give *perinaphthindandione*. J. L. D.

Phenylglutaric acids. I. $\beta\beta$ -Diphenylglutaric acid. N. L. PHALNIKAR and K. S. NARGUND (J. Univ. Bombay, 1936, 5, Part II, 105—108).— CPh_2Cl_2 and $\text{CH}_2(\text{CO}_2\text{Et})_2$ in NaOEt-EtOH give $\text{CPh}_2(\text{OEt})_2$, but with Na in C_6H_6 at 100° give crude oily $\text{Et}_4\beta\beta$ -diphenylpropane- $\alpha\gamma\gamma$ -tetracarboxylate (I), converted by NaOH-EtOH into the corresponding crude acid, m.p. 110—120°, which at 140—150° gives CO_2 and $\beta\beta$ -diphenylglutaric acid [better obtained from (I) and hot conc. HCl], m.p. 162—163° (*Ag* salt; *Me*, b.p. 210°/30 mm., and *Et*₂ ester, b.p. 253°/7 mm.; *diamide*, m.p. 172°; *dianilide*, m.p. 185°; *imide*, m.p. 188°; anhydride not obtainable). R. S. C.

Catalytic oxidation of phenanthrene by air. J. S. SALKIND and V. V. KESAREV (J. Appl. Chem. Russ., 1937, 10, 99—104).—Phenanthraquinone and solid acids [chiefly $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ (I), together with $(\text{o-C}_6\text{H}_4\text{-CO}_2\text{H})_2$ (II) and $(\text{CH}_3\text{-CO}_2\text{H})_2$ (III)] are obtained when phenanthrene (IV)-air mixtures are passed over pumice-V, -V-Mo, or -V-Mo-U catalysts, at 400°. The reaction is represented: (IV) \rightarrow (II) \rightarrow (I) \rightarrow BzOH \rightarrow (III) \rightarrow CO_2 . R. T.

Condensations of benzoylformic acids. P. DREYFUSS (Atti V Congr. Naz. Chim., 1936, 1, 358—361).—Veratroylformic acid condenses with veratrole in H_2SO_4 to 2 : 3 : 6 : 7-tetramethoxyfluorene-9-carboxylic acid. This and similar internal condensations of benzilic acids to fluorene derivatives are discussed on the basis of alternate polarities. E. W. W.

Salt effect in rearrangement of benzil-o-carboxylic acid. F. H. WESTHEIMER (J. Org. Chem., 1936, 1, 339—346).—The bimol. velocity coeff. at 100.04° for the alkali-catalysed rearrangement of benzil-o-carboxylic acid (I) increases considerably with increasing ionic strength, qualitatively in agreement with Brønsted's theory for reaction between two similarly charged ionic reactants. At high, const. ionic strength, however, in presence of K salts only, the velocity coeff. increases with increasing $[\text{KOH}]$, and differs from that obtained when the K salts are replaced by Na salts of the same ionic strength; there is no difference between NaOH and KOH at low ionic strengths (about 0.1). The rearrangement of benzil is, on the contrary, strictly bimol. with a small salt effect only. The foregoing deviations from the bimol. coeff. for the rearrangement of (I) are attributed to the medium effect. H. G. M.

New hydroxycarboxylic acid [from 4-hydroxypyrocatechol ethylene ether].—See B., 1937, 218.

Aldehydes and hydroxyaldehydes of the polymethylene series. III. Transformations of cyclopentanealdehyde. IV. Isomeric transformations of α -hydroxycyclopentanealdehyde. V. Bromo- and hydroxy-hexahydrobenzaldehyde. E. D. VENUS-DANILOVA (J. Gen. Chem. Russ., 1936, 6, 1757—1765, 1784—1795, 1863—1869).—III. *cyclopentanealdehyde* (I) and conc. H_2SO_4 at -16° yield *cyclohexanone* (II), *cyclohexylidene-* and *dicyclohexylidene-cyclohexanone*, and *dodecahydrotriphenylene*; the same products are obtained from (II)

under analogous conditions, whence it is concluded that the first product of the reaction is (II).

IV. (I) and Br in CS_2 at 0° yield the 1-*Br-derivative*, m.p. 212—215° (decomp.), converted by hydrolysis with aq. BaCO_3 into 1-*hydroxycyclopentanealdehyde* (III), b.p. 94—99°/10 mm., which with semicarbazide yields 2-*keto-6-cyclopentyl-1 : 3 : 4-triazine*, m.p. 216—218° (decomp.), and gives a *dimeride*, m.p. 96—97°, on keeping. (III) isomerises when heated with dil. H_2SO_4 (135°; 5 hr.), to yield 2-hydroxycyclohexanone, also obtained with aq. KOH and Pb(OH)_2 , or Cu(OH)_2 , at 100°. In the latter case, *cyclopentanecarboxylic acid* and its 1-OH-derivative, and 1-hydroxycyclopentylmethyl alcohol are also obtained as by-products.

V. *cyclohexanealdehyde* and Br in CS_2 yield 1-bromocyclohexanealdehyde, b.p. 87—92°/20 mm. (*trimeride*, m.p. 146—147°), converted by Ag_2O in EtOH at 80° into *cyclohexanecarboxylic acid*, and by aq. BaCO_3 into 1-*hydroxycyclohexanealdehyde* (IV), b.p. 102—108°/10 mm. (*dimeride*, m.p. 126—127°), and Δ^1 -*cyclohexenealdehyde* (V) (*semicarbazone*, m.p. 212°). (IV) yields 1-hydroxycyclohexanecarboxylic acid when oxidised (KMnO_4 in $\text{C}_5\text{H}_5\text{N}$), and a *semicarbazone*, m.p. 159—160°, with semicarbazide in aq. EtOH at 35°; at 110° the product is 2-*keto-6-cyclohexyl-1 : 3 : 4-triazine*, decomp. at 221—223°. (IV) or (V) and *p*-nitrophenylhydrazine yield 4 : 5-hexahydrobenzo-1-*p*-nitrophenylpyrazole, m.p. 184°. R. T.

Velocity of the Cannizzaro reaction. E. L. MOLT (Rec. trav. chim., 1937, 56, 233—246).—The Cannizzaro reaction with PhCHO in MeOH is termol., retarded by MeOH and accelerated by EtOH (in which solvent much MeCHO is formed). KOH and NaOH have equal effects on the velocity of the reaction, which increases 2.2 times per 10° temp. rise. *p*- $\text{OMe-C}_6\text{H}_4\text{-CHO}$ and *p*- $\text{C}_6\text{H}_4\text{Me-CHO}$ react more slowly, and *p*- $\text{C}_6\text{H}_4\text{Cl-CHO}$ more rapidly, than PhCHO . J. D. R.

Velocity of reaction of benzaldehyde with acetone and acetophenone.—See A., I, 249.

Glucovanillin and a colorimetric reaction for vanillin. W. V. THORPE and R. T. WILLIAMS (J.C.S., 1937, 494).—Vanillin (I) and β -glucose pentacetate with *p*- $\text{C}_6\text{H}_4\text{Me-SO}_3\text{H}$ or ZnCl_2 give vanillin- β -glucoside tetra-acetate, m.p. 142—143°, $[\alpha]_D^{20}$ -48.3° in CHCl_3 (2 : 4-dinitrophenylhydrazone, m.p. 202—203°), hydrolysed by NaOMe to vanillin- β -glucoside, m.p. 189—190°, $[\alpha]_D^{20}$ -86.6° in H_2O (2 : 4-dinitrophenylhydrazone, m.p. 260—264°). Of 63 phenols examined only (I) (0.002% solution) and vanillic acid give a stable purple colour or, in conc. solution, a ppt., when boiled with 2 drops of Millon's reagent. R. S. C.

Syntheses of o-homoveratraldehyde and a new method of preparing o-veratraldehyde. F. MAUTHNER (J. pr. Chem., 1937, [ii], 148, 95—100).—Guaiacol is converted by $\text{CH}_2\text{CH-CH}_2\text{Br}$ and K_2CO_3 in boiling COMe_2 into guaiacol allyl ether (I); $\text{CH}_2\text{CH-CH}_2\text{Cl}$ gives poorer yields but $\text{CH}_2\text{CH-CH}_2\text{Cl} + \text{NaI}$ is somewhat more advantageous. (I) in boiling NPhMe_2 passes into o-allylguaiacol (II), b.p. 130°/10 mm., which with NaOH and Me_2SO_4 gives o-allylveratrole, b.p. 122—123°/14 mm. This is ozonised

in anhyd. EtOAc at -20° and the ozonide is decomposed by steam with production of *o*-homoveratraldehyde [2 : 3-dimethoxyphenylacetaldehyde] (III), isolated as the *p*-nitrophenylhydrazone, m.p. $157-158^\circ$, and 2 : 3-dimethoxyphenylacetic acid (IV), m.p. $82-83^\circ$. *o*-Veratraldehyde (V), $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, and Na wire in abs. EtOH give Et 2 : 3-dimethoxyphenylglycidate, b.p. $195/14$ mm., hydrolysed and isomerised to (III), which is isolated as the oxime, m.p. $92-93^\circ$. (II) is converted by boiling NaOH-EtOH into *o*-isoeugenol, which is treated with NaOH and Me_2SO_4 and then ozonised in EtOAc at -20° to (V) in good yield. Treatment of (V) with hippuric acid and anhyd. NaOAc in Ac_2O at 100° gives the azlactone, $\text{C}_{18}\text{H}_{15}\text{O}_4\text{N}$, m.p. $169-170^\circ$, converted by NaOH and H_2O_2 into BzOH and (IV). H. W.

Reaction between toluquinone and cinnamaldehyde under the influence of light. A. ANGILETTI [with C. MIGLIARDI] (Atti V Congr. Naz. Chim., 1936, 1, 280-283).—Toluquinone and $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ in C_6H_6 exposed to light give $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, toluquinol, and 5-(or 6-)hydroxy-*o*-(or *p*-)tolyl cinnamate, m.p. 163° . E. W. W.

Oxidation of cyclohexanone and suberone by Caro's acid. R. ROBINSON and L. H. SMITH (J.C.S., 1937, 371-374).—Oxidation of suberone (improved prep.) with $\text{K}_2\text{S}_2\text{O}_8$ and H_2SO_4 in aq. EtOH, followed by treatment of the product with EtOH- H_2SO_4 , affords Et ζ -hydroxyheptate (phenylurethane, m.p. $64-65^\circ$; hydrazide, m.p. $121-123^\circ$) and (?) ε -carbethoxyhexyl ζ -hydroxyheptate, b.p. $193/0.5$ mm. By similar oxidation, cyclopentanone gives Et δ -hydroxyvalerate, b.p. $114/14$ mm. (hydrazide, m.p. $105-106^\circ$), and cyclohexanone yields Et ε -hydroxyhexoate (phenylurethane, m.p. $50-51^\circ$), reduced (Na-EtOH) to $\text{OH}\cdot[\text{CH}_2]_5\cdot\text{OH}$, δ -carbethoxymethyl ε -hydroxyhexoate, b.p. $158-160/0.05$ mm., and, in some cases, cyclohexanone peroxide, m.p. 128° . J. D. R.

Action of alkaline reagents on some nitroso- α -arylamino ketones and their oximes. J. C. EARL and S. J. HAZLEWOOD (J.C.S., 1937, 374-376).—The nitrosochlorides of ethylenic compounds are converted by primary amines into α -aminoketoximes, converted by HNO_2 into nitroso- α -aminoketoximes and hydrolysed to α -aminoketones, which with HNO_2 afford nitroso- α -aminoketones. The following are described. From methyl- Δ^1 -cyclohexene, 2-anilino-2-methyl-, m.p. 139° , and 2-nitrosoanilino-2-methyl-cyclohexanoneoxime, m.p. 148.5° , 2-anilino-2-methyl-, m.p. $91-92^\circ$, and 2-nitrosoanilino-2-methyl-cyclohexanone, m.p. 102° ; from $\text{CMe}_2\cdot\text{CHMe}$, α -nitroso-*o*-toluidino-methyl Pr^β ketoxime, m.p. 148° , α -nitroso-anilino- (I), b.p. $157/2$ mm., and -*p*-toluidino-methyl Pr^β ketone, b.p. $145/0.8$ mm.; from α -terpineol, 2-nitrosoanilino-2-methyl-5- α -hydroxyisopropylcyclohexanoneoxime, m.p. 144.5° , and from α -pinene, 2-nitrosoanilino-2 : 4 : 4-trimethyl-3 : 5-methylenecyclohexanoneoxime, m.p. 100.5° . With NaOH and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, the nitrosoanilino-ketoximes (but not ketones) afford $\text{PhN}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\cdot\beta$; the oxime of (I) also yields a substance, $\text{C}_{16}\text{H}_{24}\text{O}_3\text{N}_4$, m.p. $130-131^\circ$. J. D. R.

Synthesis of substances related to the sterols. XIV. Simple synthesis of certain octalones and

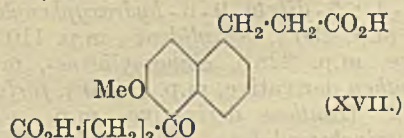
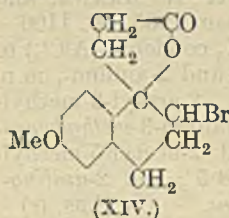
ketotetrahydrohydrindenes which may be of angle-methyl-substituted type. A theory of the biogenesis of the sterols. E. C. DU FEU, F. J. MCQUILLIN, and R. ROBINSON. XV. (IX continued.) R. ROBINSON and J. WALKER. XVI. 4-Keto-7-methoxyphenylheptonic acid and some derivatives. K. H. LIN, J. RESUGGAN, R. ROBINSON, and J. WALKER (J.C.S., 1937, 53-60, 60-67, 68-72).—XIV (Cf. A., 1935, 1498). Dicyclic ketones are obtained by condensation of cyclic ketones with substances which readily decompose giving an unsaturated ketone; alternatively the double linking may be produced in the appropriate cyclic ketone. Suitable substances ($\text{R}\cdot\text{CO}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NMeEt}_2$) I were obtained by methylation of the condensation product of the appropriate ketone ($\text{R}\cdot\text{CO}\cdot\text{R}'$) with CH_3O and NHET_2 (cf. Mannich, A., 1917, i, 634). 2-Diethylaminomethylcyclohexanone methiodide when refluxed with $\text{CHAcNa}\cdot\text{CO}_2\text{Et}\cdot\text{EtOH}$ gives 2-keto- $\Delta^{1:9}$ -octalin (I), b.p. $101-102/2-3$ mm. (semicarbazone, m.p. 208° ; 2 : 4-dinitrophenylhydrazone, m.p. 168°), also obtained by hydrolysis of Et 2-keto- $\Delta^{1:9}$ -octalin-10-carboxylate, b.p. $175-176/10$ mm., formed from Et cyclohexanone-2-carboxylate, $\text{NaOEt}\cdot\text{EtOH}$, and δ -diethylaminobutan- β -one methiodide (II). (I) is hydrogenated (H_2 -Pd-Sr CO_3) to *cis*- β -decalone (2 : 4-dinitrophenylhydrazone, m.p. $155-156^\circ$) and possibly also some of the *trans*-isomeride, and is dehydrogenated to $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$. 2-Methylcyclohexanone (III), $\text{NHET}_2\cdot\text{HCl}$, CH_3O , and cyclohexanol when heated at 110° during 2 hr. afford 2-methyl-6-diethylaminomethylcyclohexanone (IV), b.p. $95-98/3$ mm., the crude hydrochloride of which decomposes when heated giving 2-methyl-6-methylenecyclohexanone, b.p. $62/9$ mm. (condensation product, m.p. 155° , with 2 : 4-dinitrophenylhydrazine), hydrogenated to 2 : 6-dimethylcyclohexanone and dehydrogenated to *m*-2-xenol. 2 : 6-Dibenzylidenecyclohexanone is conveniently converted into 2 : 6-dibenzylphenol (V) in 75-80% yield by bubbling H_2 through a mixture with Pd-C at $200-250^\circ$ until the colour is discharged and then heating at $325-330^\circ$ (9 hr.). The 4- NO_2 -derivative, m.p. 124° (Na salt; Me ether, m.p. $70-71^\circ$), of (V) gives on reduction and subsequent oxidation 2 : 6-dibenzyl-1 : 4-benzoquinone, m.p. $76-77^\circ$; 2 : 6-di-*p*-anisylphenol, m.p. $66-67^\circ$, is similarly obtained. The methiodide of (IV) when refluxed (4 hr.) with $\text{CHAcNa}\cdot\text{CO}_2\text{Et}\cdot\text{NaOEt}\cdot\text{EtOH}$ gives 2-keto-8-methyl- $\Delta^{1:9}$ -octalin, b.p. $102/2-3$ mm. (semicarbazone, m.p. $210-211^\circ$; 2 : 4-dinitrophenylhydrazone, m.p. 172°), dehydrogenated to 1 : 7- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{OH}$. (III) when treated with NaNH_2 in Et_2O and (II) in EtOH gives 2-keto-10-methyl- $\Delta^{1:9}$ -octalin (VI), b.p. $139/15$ mm. (semicarbazone, m.p. $203.5-204^\circ$; 2 : 4-dinitrophenylhydrazone, m.p. 169°), also obtained from (III), $\text{NaOPr}^\beta\cdot\text{Pr}^\beta\text{OH}$ (or $\text{NaOEt}\cdot\text{EtOH}$), and δ -chlorobutan- β -one. (VI) is dehydrogenated (Se; $300-315^\circ$ for 4 hr. and then $330-340^\circ$ for 18 hr.) to $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, and hydrogenated (H_2 ; Pd-Sr CO_3) to 2-keto-10-methyldecalin, m.p. 47° , b.p. $95-96/3$ mm. (2 : 4-dinitrophenylhydrazone, m.p. $152-152.5^\circ$). 2-Methylcyclopentanone (VII), $\text{NHET}_2\cdot\text{HCl}$, CH_3O , and EtOH when heated (steam-bath; 4 hr.) afford 2-methyl-5-diethylaminomethylcyclopentanone, b.p. $112-114/17$ mm., the methiodide of which when

refluxed with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}\cdot\text{NaOEt}\cdot\text{EtOH}$ gives 5-keto-6-carbethoxy-3-methyl- $\Delta^{4:9}$ -tetrahydrohydri-dene, b.p. 120—125°/3 mm., hydrolysed to impure 5-keto-3-methyl- $\Delta^{4:9}$ -tetrahydrohydri-dene (semicarbazone, m.p. 196—197°; 2:4-dinitrophenylhydrazone, m.p. 159—160°). (VII) when treated with NaNH_2 , Et_2O , and (II) yields 5-keto-8-methyl- $\Delta^{4:9}$ -tetrahydrohydri-dene, b.p. 112°/4 mm. (semicarbazone, m.p. 205°; 2:4-dinitrophenylhydrazone, m.p. 153°). Similarly, *trans*- β -decalone, NaNH_2 , Et_2O , and (II) give 2-keto- $\Delta^{1:13}$ -dodecahydroanthracene, b.p. 152°/3 mm. (2:4-dinitrophenylhydrazone, m.p. 197—198°), dehydrogenated (Se; 290—300°; 6 hr.) to anthracene and β -anthranol. A plausible elaboration of the ring skeleton of the sterols from COMe_2 and CH_2O or their biological equivs. is discussed.

XV (Cf. A., 1936, 989). Et 1-keto-7-methoxy-2-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-2-carboxylate gives a homogeneous semicarbazone, m.p. 197—199°. 1-Keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene (VIII) [phenylhydrazone, m.p. 162°; semicarbazone, m.p. 238—239° (decomp.)] with $\text{Et}_2\text{C}_2\text{O}_4$ and $\text{NaOEt}\cdot\text{Et}_2\text{O}$ gives its 2-ethoxycetyl derivative ($\cdot\text{CO}\cdot\text{CO}_2\text{Et}$)₂, m.p. 90—91°, which reverts to (VIII) when heated. Me δ -keto- γ -m-methoxyphenylacetate with conc. H_2SO_4 at -10° gives Me γ -6-methoxy-3:4-dihydro-1-naphthylbutyrate, b.p. 175—178°/0.2 mm., hydrolysed by $\text{KOH}\cdot\text{MeOH}$ to the acid, which softens at 123° and collapses at 129—130° and when converted into the acid chloride and then treated with $\text{AlCl}_3\cdot\text{cyclohexane}\cdot\text{CS}_2$ gives 1-keto-7-hydroxy-1:2:3:4:9:10-hexahydrophenanthrene, m.p. 220—221°, and (VIII). Et 2-methylcyclohexanone-2-carboxylate (IX) is reduced by $\text{Al}(\text{OPr}^i)_3\cdot\text{Pr}^i\text{OH}$ giving a mixture, b.p. 118—122°/15 mm., of Et and Pr^i 2-methylcyclohexan-1-ol-2-carboxylate (3:5-dinitrobenzoate, m.p. 92—93°, of the Pr^i ester), which could not be smoothly converted into the corresponding chloride or bromide. With PCl_5 in light petroleum an unsaturated ester, b.p. 88—95°/15 mm., was obtained. Other methods for building an additional ring have been examined, and indications of reactions between (IX) and C_2H_2 in presence of K were obtained. (IX) with $\text{MgEtI}\cdot\text{Et}_2\text{O}$ gives a mixture of esters contaminated with the *sec*-alcohol produced by reduction of the keto-group of (IX). (IX) with $\text{OMe}\cdot[\text{CH}_2]_3\cdot\text{MgI}\cdot\text{Et}_2\text{O}$ gives an unsaturated substance, b.p. 129°/14 mm., and Et 2-methyl-1- γ -methoxypropylcyclohexan-1-ol-2-carboxylate, b.p. 158—168°/13 mm., dehydrated by KHSO_4 at 175° to an unsaturated compound, b.p. 140—147°/17 mm., hydrogenation of which gives an impure product, b.p. 140—144°/13 mm. (IX) with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}\cdot\text{Mg}\cdot\text{PhOMe}\cdot\text{C}_6\text{H}_6$ gives a substance, b.p. 142—152°/0.3 mm., probably Et β -6-carbethoxy-6-methyl- $\Delta^{1:2}$ -cyclohexenylpropionate, and with COMe_2 and NaNH_2 gives Et ζ -diketo- α -methyldecoate, b.p. 138—142°/0.3 mm., which boiled with $\text{NaOEt}\cdot\text{EtOH}$ gives methylcyclohexanone and a little $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$. Condensation of Me γ -methoxyphenylbutyrate (X) with γ -carbomethoxybutyryl chloride (XI) in presence of AlCl_3 in CS_2 , followed by treatment with $\text{Me}_2\text{SO}_4\cdot\text{KOH}$, gives Me γ -[5-methoxy-2-(γ -carbomethoxybutyryl)phenyl]butyrate, b.p. 205—210°/0.6 mm., cyclised when re-

fluxed with $\text{KOME}\cdot\text{C}_6\text{H}_6$ (4 hr.) to Me 1-keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene-2-carboxylate, hydrolysed to 1-keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene (A., 1935, 1499). Some 7-hydroxy-1-keto-1:2:3:4-tetrahydrophenanthrene was obtained as a by-product of cyclisation. Oxidation of 7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrol to the corresponding ketone is best achieved by means of CuO at 280—300°.

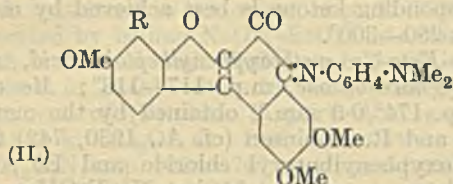
XVI. γ -Keto- ζ -m-methoxyphenylheptioic acid, m.p. 49—51° [semicarbazone, m.p. 117—118°; Me ester (XII), b.p. 174°/0.3 mm.], obtained by the method of G. M. and R. Robinson (cf. A., 1930, 742) from γ -m-methoxyphenylbutyryl chloride and Et sodioacetosuccinate, is reduced by hot $\text{Na}\cdot\text{EtOH}$ to the lactone, b.p. 178°/0.15 mm., of γ -hydroxy- ζ -m-methoxyphenylheptioic acid. (XII) when treated with H_2SO_4 at -10° gives Me β -(6-methoxy-3:4-dihydro-1-naphthyl)propionate, m.p. 60—61°, hydrolysed to the acid (XIII), m.p. 115°, which when dissolved in aq. Na_2CO_3 and treated with $\text{Br}\cdot\text{H}_2\text{O}$ gives a Br-lactone (XIV), m.p. 100°. (XIII) when heated with Pt-black is dehydrogenated to β -(6-methoxy-1-naphthyl)-propionic acid (XV), m.p. 159° (Na salt), and is reduced in MeOH by $\text{H}_2\cdot\text{Pd}\cdot\text{SrCO}_3$ to β -(6-methoxy-1:2:3:4-tetrahydro-1-naphthyl)propionic acid (XVI), m.p. 77°, the Me ester of which does not react with (XI) in presence of AlCl_3 . (XII) when treated at 0° with $\text{AlCl}_3\cdot\text{CS}_2$ yields (XIII), (XV), and (XVI), but when treated at 0° with excess of (XI) in presence of $\text{AlCl}_3\cdot\text{CS}_2$ and then with $\text{Me}_2\text{SO}_4\cdot\text{NaOH}$ gives (XV) and the acids, $\text{C}_{19}\text{H}_{20}\text{O}_6$, m.p. 210°, and $\text{C}_{19}\text{H}_{24}\text{O}_6$, m.p. 144°. Both acids are stable to KMnO_4 and react with 2:4-dinitrophenylhydrazone, but only the former is unaffected by boiling $\text{Ac}_2\text{O}\cdot\text{NaOAc}$, and probably is (XVII). Treatment of (X) and phenyl-



ethylcarbamy chloride with AlCl_3 in CS_2 followed by hydrolysis of the product affords γ -(2-carboxy-5-methoxyphenyl)butyric acid, m.p. 173° after sintering at 165°, which when boiled with Ac_2O is converted into 6-methoxytetralone. The prep. of γ -cyano- α -methylbutyrate (cf. J.C.S., 1900, 77, 947) and its conversion into γ -carbethoxyvaleryl chloride, b.p. 134—142°/15—16 mm., are described. γ -Carbethoxyvalero- β -naphthylamide has m.p. 76.5—77.5°. H. G. M.

Behaviour of open and cyclic ketones towards nitroso-compounds. P. PFEIFFER and H. BÖTTCHER (J. pr. Chem., 1937, [ii], 148, 126—134; cf. A., 1935, 1369).—Treatment of $\text{COMe}\cdot\text{CH}_2\text{Ph}$ with $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ and KOH gives benzylidene- p -dimethylaminoaniline (I), m.p. 99—100°, whilst indecisive results are obtained with PhNO . (I) accompanied by $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ is also obtained from

p -NO-C₆H₄·NMe₂ and CO(CH₂Ph)₂; similar results are obtained with CH₂PhBz and CH₂Ph·CO·CH₂·O·C₆H₄·OMe- p . CO(CH₂Ph)₂ and PhNO give NHPbBz and CH₂Ph·CO₂H, whilst NHPbBz accompanied by BzOH and p -OMe·C₆H₄·O·CH₂·CO₂H, respectively, are derived from CH₂PhBz and CH₂Ph·CO·CH₂·O·C₆H₄·OMe- p . Trimethylbrasilon is converted by p -NO-C₆H₄·NMe₂



into the compound (II, R = H), converted by α -C₆H₄(NH₂)₂ into the phenazine derivative, C₂₅H₁₈O₄N₂, m.p. 261·5°. Similarly, tetramethylhematoxylone yields the anil (II; R = OMe) transformed into the phenazine derivative, C₂₆H₂₀O₅N₂, m.p. 279°. H. W.

Condensation of acetoanthranil derivatives with benzene. M. HAYASHI, H. NAMIKAWA, and I. MORIKAWA (J. Chem. Soc. Japan, 1935, 56, 1106—1111).—Acetylthranil and C₆H₆ condense (AlCl₃) to yield 2-amino-, m.p. 109—110°, and 2-anilino-, m.p. 121·5—122°, -benzophenone; 2-acetyl-3-methylanthranil similarly affords 2-anilino-3-methylbenzophenone, m.p. 123—123·5°, and 2-acetyl-5-methylanthranil, 2-amino-, m.p. 64—64·5°, and 2-anilino-, m.p. 163·5°, -5-methylbenzophenone. CH. ABS. (r)

Dihydroresorcinols. IV. Condensation of phenyldihydroresorcinol with aromatic aldehydes. R. D. DESAI and M. A. WALI (J. Indian Chem. Soc., 1936, 13, 735—739).—In presence of C₅H₁₁N, phenyldihydroresorcinol (I) with the appropriate aldehyde gives the bis-derivative, dehydrated to the xanthen derivative: *salicylidene*-, m.p. 169—170° (Ac derivative, m.p. 145°; 2:7-diphenyl-4:5-diketo-9-o-hydroxyphenyloctahydro-xanthen, m.p. 230°), *benzylidene*-, m.p. 110° (xanthen derivative, m.p. 228°), *cinnamylidene*-, m.p. 155—156° (xanthen derivative, m.p. >280°), *furfurylidene*-, m.p. 122° (xanthen derivative, m.p. >280°), *p*-dimethylaminobenzylidene-, m.p. 107—108° (xanthen derivative, m.p. 200°), 3:4-methylenedioxybenzylidene-, m.p. 148° (xanthen derivative, m.p. >280°), 4-hydroxy-3-methoxybenzylidene-, m.p. 116° (xanthen derivative, m.p. >280°), and *o*-nitrobenzylidene-bisphenyldihydroresorcinol, m.p. 160° (xanthen derivative, m.p. 272°). (I) and *o*-OH·C₆H₄·CHO with HCl yield 2-phenyl-4-keto-1:2:3:4-tetrahydrobenzopyranol anhydrochloride, m.p. >360° (anhydrobase, m.p. >360°). With chloral hydrate, (I) yields 1-phenyl-4-(α -hydroxy- $\beta\beta$ -trichloroethyl)cyclohexane-3:5-dione, m.p. 145—146°, and with SOCl₂ affords the oxide of 2:7-diphenyl-4:5-diketo-1:2:3:4:5:6:7:8-octahydrophenothioxin (?), m.p. 216°. Similarly dimethyldihydroresorcinol gives the oxide of 2:2:7:7-tetramethyl-4:5-diketo-1:2:3:4:5:6:7:8-octahydrophenothioxin (?), m.p. 181—182°, 1:1-dimethyl-4-(α -hydroxy- $\beta\beta$ -trichloroethyl)cyclohexane-3:5-dione, m.p. 120°, and

furfurylidene-, m.p. 160° (xanthen derivative, m.p. >280°), and *p*-dimethylaminobenzylidene-bisdimethyldihydroresorcinol, m.p. 114° (xanthen derivative, m.p. 220°). F. R. S

Transformation of oximinoacetophenone. F. ANGELICO and S. CUSMANO (Gazzetta, 1936, 66, 791—796).—COPh·CH·N·OH (I) boiled with dil. HCl gives the substance, C₁₆H₁₂O₃N₂ (II), m.p. 220°, which is obtained from BzCHO and NH₂OH·HCl (A., 1890, 51), and by other methods (A., 1901, i, 549, etc.). This, previously regarded (A., 1891, 287) as O<CHBz>N:CPh>C·N·OH (III) or, improbably, as O<CBz·N>CPh·OH (A., 1907, i, 1086), is now regarded as 4-oximino-3-benzoyl-5-phenyl-4:5-dihydroisooxazole, O<N:CBz>CHPh>C·N·OH, and as being derived from 2 mols. of (I). BzCHO and NH₂OH·HCl do not give OH·CHBz·COBz [formerly regarded (A., 1897, i, 497) as an intermediate to structure (III), and now found not to yield (II) with NH₂OH·HCl], but (I) and (II). Phenylglyoxime and dil. HCl also give (I). E. W. W.

Manufacture of 3:5-di-iodo-4-hydroxyacetophenone and its derivatives substituted in the hydroxyl group.—See B., 1937, 218.

Chelation. V. Hydroxyacetylhydrindene. W. BAKER. VI. Hydroxy-derivatives of acetylnaphthalenes, benzonitrile, and carboxylic esters. W. BAKER and G. N. CARRUTHERS (J.C.S., 1937, 476—479, 479—483; cf. A., 1936, 727).—V. Fixation of the ethylenic linkings in hydrindenes is confirmed by the fact that 5-hydroxy-6- (I) is more fully chelated than 5-hydroxy-4-acetylhydrindene (II); both are chelated, but (I) is more sol. in C₆H₆ and light petroleum, and (I) is volatile and (II) non-volatile in steam. The prep. of 5-acetylhydrindene, its oxime, 5-acetamido-, 5-amino-, and thence 5-hydroxyhydrindene (III) is described. 5-Acetoxyhydrindene, b.p. 136°/18 mm., and AlCl₃ in CS₂ give readily (I), m.p. 59° (Ac derivative, m.p. 88°; Cu salt, sol. in CHCl₃). 6-Bromo-5-acetoxyhydrindene, b.p. 169°/16 mm., and AlCl₃ in CS₂ give slowly 6-bromo-5-hydroxy-4-acetylhydrindene, m.p. 102—103°, stable to KOH-EtOH at 100°, and, in one case, an isomeride, m.p. 115°, both converted by Zn-2% NaOH into (II), m.p. 124·5° (Cu salt, sol. in CHCl₃).

VI. 2:1-, m.p. 101°, 1:2-, m.p. 64°, and 2:3-C₁₀H₆Ac·OH (IV), m.p. 112° (preps. described), are much more chelated than the 1:4 compound. (IV) gives a (? 1-)Br-derivative, m.p. 150°, and does not add maleic anhydride. Its chelation shows it to contain abnormally a C₁₂₋₃ ethylenic linking, possibly explicable by resonance. *o*-, *m*-, and *p*-OH·C₆H₄·CN are not chelated, probably owing to the linear nature of the CN. Et₂ quinol-2:3-dicarboxylate, m.p. 85°, is surprisingly less chelated than the 2:5-dicarboxylate, m.p. 133°, and Et₂ resorcinol-4:6-dicarboxylate, new m.p. 140°; for this also resonance may provide an explanation. R. S. C.

Application of 2-nitroindan-1:3-dione to the isolation and identification of organic bases. G.

WANAG and A. LODE (Ber., 1937, 70, [B], 547—559).—2-Nitroindan-1 : 3-dione (I) yields salts with the following bases, usually obtained from the hydrochloride of the bases and (I) in H₂O or EtOH: NH₂Me, m.p. 203—205°; NH₂Et, m.p. 203°; NH₂Pr^a, m.p. 184—185°; NH₂Bu^g, m.p. 178°; *n*-heptylamine, m.p. 149—150°; *n*-heptadecylamine, m.p. 118—119°; allylamine, m.p. 180—181°; CH₂Ph·NH₂, m.p. 180°; CHPhMe·NH₂, m.p. 207°; CH₂Ph·CH₂·NH₂, m.p. 169°; CHPh₂·NH₂, m.p. 205°; cyclohexylamine, m.p. 213°; camphylamine, m.p. 169°; bornylamine, m.p. 211°; C₂H₄(NH₂)₂, m.p. 204—205°; NHMe₂, m.p. 210°; NHEt₂, m.p. 180—181°; NHP^a₂, m.p. 210°; NHBu^g₂, m.p. 231°; diisoamylamine, m.p. 190°; NH(CH₂Ph)₂, m.p. 203°; NMe₃, m.p. 162°; NEt₃, non-cryst.; NBu^g₃, m.p. 111°; *o*-, m.p. 183°, and *p*-C₆H₄Et·NH₂, m.p. 181°; 1 : 3 : 4-, m.p. 192°, 1 : 3 : 2-, m.p. 185°, 1 : 4 : 2-, m.p. 196°, and 1 : 3 : 5-, m.p. 218°; -xylidine; *o*-, m.p. 183°, and *m*-C₆H₄Ph·NH₂, m.p. 198° (much decomp.); α -, m.p. 209—210°, and β -C₁₀H₇·NH₂, m.p. 193°; α -aminofluorene, m.p. 195°; *o*-, m.p. 172—174°, *m*-, m.p. 200°, and *p*-C₆H₄(NH₂)₂, m.p. 261—263°; *p*-NH₂·C₆H₄·NHAc, m.p. 212°; 1 : 2 : 4-tolylene-diamine, m.p. 183°; benzidine, decomp. 213°; *o*-tolidine, m.p. 216°; CH₂(C₆H₄·NH₂)₂·4 : 4', m.p. 248°; 2 : 7-diaminofluorene, m.p. 240° (indef.); NHP^aEt, m.p. 183°; NHP^aPr^a, m.p. 190—191°; NHP^aBu^a, m.p. 209°; NHP^aBu^g, m.p. 207°; *o*-C₆H₄Me·NHMe, m.p. 190°; *o*-, m.p. 192°, and *p*-C₆H₄Me·NHMe, m.p. 164°; *o*-C₆H₄Me·NMe₂, m.p. 150°; *p*-C₆H₄Me·NMe₂, m.p. 149°; α -C₁₀H₇·NMe₂, m.p. 153°; *ar*-tetrahydro- α -naphthylamine, m.p. 204°; *ac*-tetrahydro- β -naphthylamine, m.p. 233°; C₅H₅N, m.p. 168°; α -picoline, m.p. 161°; collidine, m.p. 146°; piperidine; quinoline, m.p. 155°; quinaldine, m.p. 157°; 8-methylquinoline, m.p. 160°; acridine, m.p. 183°; 2-aminopyridine, m.p. 197°; quinine, m.p. 186°; strychnine, m.p. 226° (indef.); brucine, m.p. 185°; acetamidine, m.p. 240°; benzamidine, m.p. 195°; guanidine, m.p. 258° (indef.). H. W.

Action of bromine on phenyl *o*-hydroxystyryl ketone. A. MANGINI (Gazzetta, 1937, 67, 39—46).—This ketone and Br in MeOH or AcOH give *Ph* α - β -dibromo- β -3 : 5-dibromo-2-hydroxyphenylethyl ketone (I), m.p. 152° (decomp.) (cf. A., 1896, i, 302), oxidised (KMnO₄-H₂O) to BzOH or (KMnO₄-COMe₂) to 3 : 5-dibromosalicylic acid. With KOH-MeOH, (I) is converted (rate of debromination studied) into 5 : 7-dibromo-2-benzoylcoumarone, m.p. 167—169° (oxime, m.p. 200—200.5°; *p*-nitrophenylhydrazone, m.p. 248—249°), also obtained from 3 : 5-dibromosalicylaldehyde (prep. improved) and CH₂BzBr.

E. W. W.

Syntheses of 2-acetylresorcinols by the Nidhone process. II. 2-Acetylresorcinol. Proof of its constitution. D. B. LIMAYE and D. D. GANGAL (Rasāyanam, 1936, 1, 64—68; cf. A., 1934, 298).—The orientation of 2-acetylresorcinol [prep. from 8-acetyl-4-methylumbelliferone (I)], m.p. 157° (*Me* ether, m.p. 60°; semicarbazone, m.p. 220°; phenylhydrazone, m.p. 153°; Bz₂ derivative, m.p. 106°), is proved by oxidation of its *Me*₂ ether, m.p. 73°,

by KMnO₄ to 2 : 6-dimethoxyphenylglyoxylic acid, +H₂O, m.p. 98° [semicarbazone, m.p. 210° (decomp.)], and thence by H₂O₂ to 2 : 6-(OMe)₂C₆H₃·CO₂H. This proves also the structure of (I) and of 8-acetyl-7-carbethoxymethoxy-4-methylumbelliferone and the derived acid, m.p. 212°, and ang.-3' : 4-dimethyl-7 : 8-furocoumarin (II), m.p. 177°, derived therefrom.

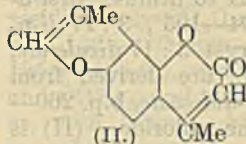
R. S. C.

Sexual hormones. XX. Preparation of oxides from Δ^5 -cholestenone and Δ^5 -androstenedione. XXI. Doubly unsaturated ketones of the androstane series. L. RUZICKA and W. BOSSHARD (Helv. Chim. Acta, 1937, 20, 244—249, 328—332).—XX. Cholesterol (I) is oxidised by BzO₂H in CHCl₃ at room temp. to α -cholesterol oxide, m.p. (impure) 137°, oxidised by CrO₃ in AcOH to 5-hydroxycholestane-3 : 6-dione, m.p. 246—248°, converted at 250° into Δ^4 -cholestene-3 : 6-dione, m.p. 132°. Cholesteryl acetate is transformed by BzO₂H in CHCl₃ into the corresponding oxide, m.p. 111—112°, converted by HCl in CHCl₃ into 6-chloro-5-hydroxy-3-acetoxycholestane, m.p. 191°. (I) is transformed into the dibromide, which is oxidised and then debrominated by NaHCO₃ and Zn dust in boiling EtOH to Δ^5 -cholesten-3-one. This is oxidised by BzO₂H to α -, m.p. 202°, and β -, m.p. 122°, 5 : 6-oxidocholestan-3-one, the latter of which is hydrolysed by 2N-H₂SO₄ in dioxan to cholestane-3 : 6-dione. Δ^5 -Androstenedione gives 5 : 6-oxidoandrostane-3 : 17-dione, m.p. 265°.

XXI. *trans*Dehydroandrosterone is transformed by Br in AcOH into the dibromide, which when boiled with anhyd. NaOAc in abs. EtOH gives 6-bromo-androstenedione, converted by boiling anhyd. C₅H₅N into Δ^4 : 6-androstadiene-3 : 17-dione (III), m.p. 173° (corr.). Similarly, Δ^5 -androstenediol 17-monobenzoate is transformed into 6-bromotestosterone benzoate, m.p. 176—177° (corr.), and thence into dehydrotestosterone benzoate, m.p. 246° (corr.). Δ^5 -Androstene-3-*trans*-17-diol 17-propionate analogously gives Δ^6 -dehydrotestosterone propionate, m.p. 134° (corr.). H. W.

Biochemical transformation of Δ^4 -androstenedione into Δ^4 -testosterone. Genesis of the male sexual hormone. L. MAMELI and A. VERCELLONE (Ber., 1937, 70, [B], 470—471).—Addition of Δ^4 -androstenedione in EtOH to a fermenting mixture of sugar and yeast gives Δ^4 -testosterone. H. W.

Esters of the follicle hormone series. K. MIESCHER and C. SCHOLZ (Helv. Chim. Acta, 1937, 20, 263—271).—Estrone (I) is transformed by the requisite acid anhydride in hot C₅H₅N into the propionate, m.p. 134—135.5°, *n*-butyrate, m.p. 101—102.5°, and valerate, m.p. 100—101°; the decanoate, m.p. 71—71.5°, and palmitate, m.p. 75.5—76°, are obtained by use of the acid chloride in C₅H₅N at room temp. Estrone acetate (II) is converted by the Adams catalyst in EtOH into (I); the change appears due to adsorbed alkali since it is not observed



(II.)

if the catalyst suspension, after pre-reduction, is exactly neutralised by HCl-EtOH to litmus. *Estradiol 3:17-dipropionate*, m.p. 104—105°, *3:17-di-n-butyrate*, m.p. 64—65°, and non-cryst. *3:17-divalerate*, b.p. 220—230° (bath)/0.05 mm., are derived from the acid anhydride and the *3:17-didecoate*, b.p. 260—265° (bath)/0.001 mm., from the chloride. (II) is reduced (PtO₂ in EtOAc) to *estradiol 3-acetate*, m.p. 136.5—137.5°; the *3-propionate*, m.p. 124.5—125.5°, and *3-palmitate*, m.p. 69—71°, are obtained analogously. *Estradiol 17-acetate*, m.p. 215—217.5°, is obtained by shaking the diacetate in abs. EtOH at room temp. with freshly reduced PtO₂ catalyst containing alkali. The *17-monopropionate*, m.p. 198—200°, is obtained similarly, by the action of K₂CO₃ in 90% MeOH or of 0.5N-HCl-EtOH. The *17-monobutyrate* has m.p. 166.5—167°. *Estradiol 3-benzoate* is transformed by the requisite acid anhydride in C₆H₅N at 100—105° into *estradiol 3-benzoate 17-acetate*, m.p. 172—173°, *17-propionate*, m.p. 167—167.5°, and *17-n-butyrate*, m.p. 128.5—129°. The physiological action of the hormone can be greatly increased by suitable esterification. H. W.

Oxonium compounds. Complexes of quinones with hydrochloric, phosphoric, and acetic acids, and their chlorination. V. V. TSCHELINEV (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 289—291).—Benzoquinone forms dioxonium salts in conc. acids and its reactions are influenced by this fact. Thus, Cl₂ in CHCl₃ gives indefinite products: at 0° a substance, m.p. 102°, and at 10° a substance (Cl 19.84%), m.p. 122°. In HCl 2:3-di- (I) (*diphenylimide*) or tetra-chlorobenzoquinone (II), or benzoquinone tetrachloride, m.p. 226°, is formed according to the concn. of HCl. In 86% H₃PO₄ (I) is formed more slowly, but in H₃PO₄-HCl chlorination proceeds further. In AcOH a polychloro-compound, m.p. 272°, is formed, and in AcOH-HCl probably (II).

R. S. C.

Phenoquinones. M. COVELLO (Atti V Congr. Naz. Chim., 1936, 1, 337—345).—The action of PhOH or of quinol on 2:6-dipthalimidobenzoquinone (I) in AcOH, EtOH, or COMe₂ is studied; quinhidrone and 2:6-dipthalimidoquinol are isolated, but no phenoquinones are obtained. This supports the view that in the latter the phenol has become attached to the nucleus, and not to the 1:4 O atoms, which in (I) are free to react. E. W. W.

Review of the semiquinone problem. L. MICHAELIS (Trans. Electrochem. Soc., 1937, 71, Preprint 17, 185—201).—A review of the evidence for two-stage oxidation-reduction processes of quinonoid substances, and its significance in biology.

H. J. E.

Dyes of the anthracene group and their photosensitive capacity.—See A., I, 169.

Spectrographic and chemical study of some aliphatic terpenes. I. Myrcene and its hydrogenation products. G. DUPONT and V. DESREUX (Bull. Soc. chim., 1937, [v], 4, 422—435).—Mainly a detailed account of work already reported (A., 1936, 1514; this vol., 27). A fraction of lemongrass oil, believed to be methylheptenone, was >50% β -myrcene (I), the purification of which is detailed.

With H₂-PtO₂ no H₂-product could be isolated from (I), 2 H₂ being absorbed *en bloc*. Structures are determined mainly by Raman spectra. R. S. C.

Citronellal-terpene. I. Existence of a new terpene, C₁₀H₁₆. H. OTSUKI (J. Chem. Soc. Japan, 1935, 56, 1213—1220).—With 50% H₂SO₄ at room temp. citronellal affords *monogene*, C₁₀H₁₆, b.p. 184—186°, [α]_D²⁰ +49.11° (*nitrosate*, m.p. 154.5—155.5°), which may be $\Delta^{2:4(8)}$ -*p*-menthadiene. CH. ABS. (r)

Isomeration and hydration of pinene. R. W. CHARLTON and A. R. DAY (Ind. Eng. Chem., 1937, 29, 92—95).—Terpinolene, terpineol, terpene hydrate, dipentene (I) and *p*-cymene are identified amongst the acid (H₂SO₄-EtOH) isomerisation and hydration products of α -pinene (II). The vapour-phase isomerism of (II) (ThO₂; 380—425°) affords 55—65% of (I) and camphene. F. N. W.

Constitution of sulphocamphylic acid. J. R. LEWIS and J. L. SIMONSEN (J.C.S., 1937, 457—459).—Bromodihydro- β -camphylic acid (Perkin, J.C.S., 1898, 73, 827; improved prep.) is 4-bromo-2:3:3-trimethyl- Δ^1 -cyclopentenecarboxylic acid, since O₃-EtOAc at 0° converts it into liquid CMe₂Ac·CHBr·CH₂·CO₂H (*semicarbazone*, m.p. 190°), further oxidised by NaOBr at 0° to CHBr₃ and *trans*- α -dimethylglutaconic acid. Sulphocamphylic acid (I) is therefore 4-sulpho-2:3:3-trimethyl- Δ^1 -cyclopentene-1-carboxylic acid, and its oxidation product, sulphopimelic acid, is β -sulpho- α -dimethylglutaric acid, converted by pyrolysis at 160—170°/reduced pressure into a mixture of *cis*- and *trans*-CO₂H·CMe₂·CH·CH·CO₂H, and not, as stated by Koenigs *et al.* (A., 1893, i, 363; 1894, i, 47), into terebic acid. (I) with O₃ gives an oil (CHBr₃ with NaOBr), converted by heating at 130—140° into an acid, C₁₆H₂₀O₄, m.p. 145—147°. Ozonolysis of the Me ester of (I) gives an *ozonide*, m.p. 83—85°, from which no cryst. products could be isolated.

J. W. B.

Reactivities of α - and β -campholides. Preparation of the corresponding hydroxycampholic acids. F. SALMON-LEGAGNEUR and J. VENE (Bull. Soc. chim., 1937, [v], 4, 448—462).—When α - and β -campholide (modified preps.) are heated with alkali, cooled, and then treated with acid (excess avoided; Congo-red), α -, m.p. 119°, [α]_D²⁰ +56.8° in EtOH, and β -hydroxycampholic acid, m.p. 116—117°, [α]_D²⁰ +54.8° in EtOH, are obtained. The rate of hydrolysis of the α -lactone is 4 times that of the β -lactone. The rate of lactonisation of the β -acid is 7 times that of the α -acid, H⁺ being a potent catalyst. R. S. C.

Optical activity and chemical constitution. III. Optically active acids and bases. MAHAN SINGH and MANOHAR SINGH (J. Indian Chem. Soc., 1936, 13, 744—746).—Camphoric anhydride and aminodimethylanilines condense to 4'-, m.p. 193° 3', m.p. 120°, and 2'-dimethylaminocamphoranilic acid, m.p. 152—153°, and camphoro-o-dimethylaminophenylimide (I), m.p. 149°. The rotatory powers of these substances have been determined in MeOH, EtOH, and COMe₂. The addition of HCl to the 2'-acid increases [α] considerably; addition of HCl to the 4'-acid decreases, and that of NaOH slightly increases, [α]. In MeOH,

$[\alpha]_D$ is: 4' - +69.82°; 3' - +55.7°; 2'-acid 0°; (I), +14.35°. F. R. S.

Contact changes of camphor. Y. FUJITA (J. Chem. Soc. Japan, 1935, 56, 1210—1212).—Camphor vapour passed through a Cu tube containing active C at 480—500° gives carvenone, carvacrol, *o*-cresol, *p*-cymene, and cumene. CH. ABS. (r)

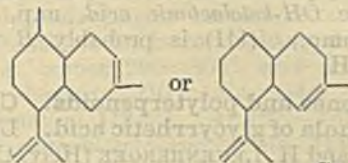
Sulphonation of camphor. Y. ASAHINA [in part with K. YAMAGUTI] (Proc. Imp. Acad. Tokyo, 1937, 13, 38—40).—The formation of camphor- ω -sulphonic acid (I) is explained as due to addition of H_2SO_4 to the $C:CH_2$ of 1-hydroxycamphene (II), derived through a retropinacolin inversion of camphor in the *o*-ketonic form; (I) can be prepared in good yield from (II). Formation of camphor- π -sulphonic acid is ascribed to addition of H_2SO_4 to 4-hydroxycamphene (formed by interchange of OH with a *gem*-Me, followed by loss of H_2O), after which the *gem*-Me migrates back, with ring-isomerisation. The racemisation of camphor, but not of α -bromocamphor, during sulphonation, is ascribed to hindrance by the Br of addition of H_2SO_4 to the camphor-enol, which, it is suggested, precedes a Wagner change. E. W. W.

Reduction products of 2:6-diketocamphane. Y. ASAHINA and T. TUKAMOTO (Ber., 1937, 70, [B], 584—588).—Reduction of 2:6-diketocamphane (I) with Zn dust in well-cooled HI gives only 6-hydroxycamphor, m.p. 130°, $[\alpha] \pm 0^\circ$ in EtOH (semicarbazone, m.p. 200°), purified through the 3:5-dinitrobenzoate, m.p. 146°, and oxidised by CrO_3 in AcOH to α -campholonic acid (II). Reduction of 2:6-diketocamphanedioxime (Pd-C in AcOH) affords 2:6-diketocamphane-monoxime, m.p. 170°, converted by dil. KOH into the oxime of (II) and by $NH_2 \cdot CO \cdot NH \cdot NH_2$ into the oxime-semicarbazone, m.p. 219°, of (I). (I) with Zn dust and HI gives the ketimine hydriodide, $C_{10}H_{18}N_2I_2$, m.p. 232—235°, converted by the successive action of alkali and warm dil. HCl into (II). α -Nitrocamphene (III) is transformed by KOH-EtOH into isonitrocamphene (III), m.p. 114° (corresponding *p*-nitrole, m.p. 112—113°), which immediately decolorises $KMnO_4$ and passes when melted into (IV). Oxidation of (III) gives α -camphenone (V), the semicarbazone, m.p. 213.5°, of which is converted by NaOEt-EtOH at 160° into camphene. (V) with 95% HCO_2H at 120—125° affords hydroxydihydro- β -campholenolactone, m.p. about 35°, and with Na-EtOH it yields 6-hydroxycamphene (VI), m.p. 114°. Attempted hydration of (VI) by 50% H_2SO_4 in AcOH at 60° leads to 6-acetoxycamphene, b.p. 70—72°/14 mm., and a substance, b.p. 180°/14 mm., which is stable to $KMnO_4$, decolorises Br in $CHCl_3$, and is probably a product of the polymerisation of α -hydroxycamphene. H. W.

Reversal of optical rotation in the camphene rearrangement. S. S. NAMETKIN and A. I. SCHAVRIGIN (J. Gen. Chem. Russ., 1937, 7, 3—5).—Polemical in reply to Houben *et al.* (A., 1936, 729). R. T.

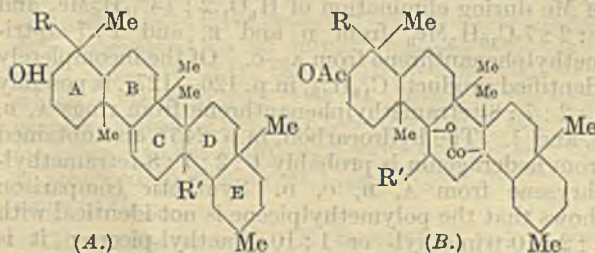
Essential oil of *Lantana camara*, L. II, III. K. KAFUKU, T. IKEDA, and C. HATA (J. Chem. Soc. Japan, 1935, 56, 1184—1191).—From the oil are isolated *camerene* (I), b.p. 263°, n_D^{20} 1.500, $[\alpha]_D^{27} + 6.74^\circ$, oxidation of which (O_3) yields CH_2O and $COMe_2$

and a non-volatile residue containing succinic acid isocamerene, b.p. 253°, n_D^{20} 1.4925, $[\alpha]_D^{27} - 11.21^\circ$ yielding only CH_2O on oxidation, and *micranene* (II), b.p. 126—8°/5 mm., n_D^{20} 1.5050 (*hydrochloride*, m.p. 105.5—106.5°), which on oxidation (O_3) gives CH_2O and $COMe_2$, and a residue yielding a salt $C_{14}H_{21}O_4Ag$ or, with $KMnO_4$, hexahydromellophanic acid. (II) is probably



CH. ABS. (p)

Polyterpenes and polyterpenoids. CX. Transformation of gypsogenin into hederagenin. L. RUZICKA and G. GIACOMELLO (Helv. Chim. Acta, 1937, 20, 299—309; cf. A., 1936, 1514).—The more freely sol. acetate, m.p. 176—177°, from gypsogenin (I) now designated *acetylgyssogenin* (II) is transformed by HCl-AcOH at 100° into *isoacetylgyssogeninolactone*, m.p. 331—332° (decomp.), $[\alpha]_D^{20} + 33^\circ$, and is hydrolysed by conc. HCl in MeOH- $CHCl_3$ to (I), which, like the original material, has m.p. 268—271° (corr.) after softening at 240° and from which by sublimation at 210°/high vac. a small amount of material, m.p. 272—276° (corr.), is derived. Analyses of this material, which is monobasic, agree well with the formula $C_{30}H_{46}O_4$. The sparingly sol. acetate, m.p. 262° (*loc. cit.*), now termed "*acetylgyssogeninolactone*" (III), is neutral and is formed in small amount when (II) is boiled with MeOH or EtOH; it gives non-cryst. products when hydrolysed. Oxidation of the Br-lactone (*loc. cit.*) of (II) in AcOH by CrO_3 in presence of H_2SO_4 yields an acid, $C_{32}H_{47}O_5Br$, m.p. >310° (corr.; decomp.) [*Me ester*, m.p. 238—240° (corr.; decomp.)]. (I) therefore contains $\cdot CHO$. It is oxidised to hederagone so that it is a dehydrohederagenin containing $\cdot CHO$ in place of $\cdot CH_2 \cdot OH$. This conclusion is confirmed by the catalytic reduction of (I) to hederagenin (IV). The conversion of (I) into oleanolic acid (V) and (IV) and Zimmermann's oxidation of erythrodil (VI) to (V) establish the close relationship of the four natural triterpenes, which are stereochemically alike and differ in the structure of two side-chains. The structure A is therefore advanced [(I), $R = CHO$, $R' = CO_2H$; (V), $R = Me$, $R' = CO_2H$; (VI), $R = Me$, $R' = CH_2 \cdot OH$; (IV), $R = CH_2 \cdot OH$, $R' = CO_2H$]. (II) is oxidised by H_2O_2 to a *OH-lactone* (VI) (B ; $R = CHO$, $R' = OH$), m.p.



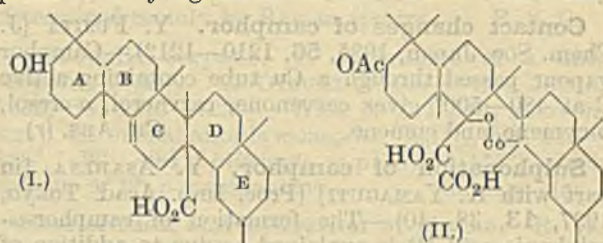
276—278° (corr.; decomp.), which is neutral, does not give a yellow colour with $C(NO_2)_4$, and gives a Ac_2 derivative, m.p. 226—228° (corr.). (VI) is oxid-

ised by CrO_3 in AcOH to the *ketolactone* (*B*; $\text{R} = \text{CHO}$, $\text{R}' = \text{:O}$), m.p. 245° (corr.; decomp.), $[\alpha]_D^{25} +29^\circ$ in CHCl_3 [*dioxime*, m.p. 226° (corr.; decomp.)], and by CrO_3 in presence of H_2SO_4 to the *acid* (*VII*) (*B*; $\text{R} = \text{CO}_2\text{H}$; $\text{R}' = \text{:O}$), m.p. $309\text{--}311^\circ$ (corr.), which neutralises 3 mols. of KOH in boiling EtOH , and gives an *oxime*, m.p. $239\text{--}240^\circ$ (corr.; decomp.), and a *Me* ester, m.p. $277\text{--}280^\circ$ (corr.); (*VII*) is hydrolysed to the *OH-ketolactonic acid*, m.p. $329\text{--}332^\circ$ (corr.; decomp.). (*III*) is probably *B* with $\text{R} = \text{CHO}$, $\text{R}' = \text{H}$. H. W.

Polyterpenes and polyterpenoids. CXI. Empirical formula of glycyrrhetic acid. L. RUZICKA, M. FURTER, and H. LEUENBERGER (Helv. Chim. Acta, 1937, 20, 312—325; cf. this vol., 68).—New analytical data confirm the formula $\text{C}_{30}\text{H}_{46}\text{O}_4$ for glycyrrhetic acid (*I*). The authors' results are considered in conjunction with those of Voss *et al.* (this vol., 87) and Bergmann *et al.* (A., 1934, 328; this vol., 203). Hydrolysis of glycyrrhizin to (*I*) is readily achieved with conc. HCl at 50° . (*I*) is isolated in two forms which are regarded as cryst. modifications, not isomerides. Analyses are recorded of (*I*), its *Me* ester (*II*), acetylglycyrrhetic acid (*III*) and its *Me* ester (*IV*). Prolonged hydrolysis of (*II*) or (*IV*) with 0.1*N*- and 0.5*N*- KOH - EtOH give the vals. leading to the formula $\text{C}_{30}\text{H}_{46}\text{O}_4$ when the more conc. alkali is used; with the dil. alkali a part of the ester remains intact. Titrations of (*I*) and (*III*) also establish $\text{C}_{30}\text{H}_{46}\text{O}_4$ for (*I*). Rast's method of determining the mol. wt. is regarded as inapplicable to (*I*) on account of its very sparing solubility and re-calculation of Bergmann's röntgenographic data leads to the val. 468.8 ± 24 , in good agreement with the calc. val. for $\text{C}_{30}\text{H}_{46}\text{O}_4$. (*I*) does not give a semicarbazone or oxime and (*III*) is unchanged when boiled with Ac_2O and $\text{C}_5\text{H}_5\text{N}$. (*I*) does not accept O when titrated with BzO_2H . Since a double linking has not been detected in (*I*) the presence of 6 rings is probable. (*I*) is dehydrogenated by Se to sapotalin, $2:7\text{-C}_{10}\text{H}_6\text{Me}_2$, and a polymethylpicene, m.p. 306° . H. W.

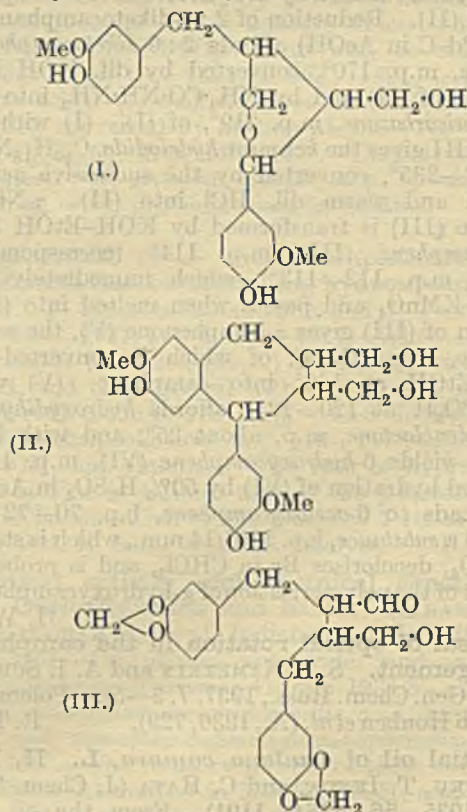
Polyterpenes and polyterpenoids. CXII. Structure of the rings C—E of the pentacyclic triterpenes. L. RUZICKA, M. W. GOLDBERG, and K. HOFMANN (Helv. Chim. Acta, 1937, 20, 325—328).—The modified constitution (*I*) is advanced for oleanolic acid. Of the isolated and identified products of dehydrogenation $1:2:3:4\text{-C}_6\text{H}_2\text{Me}_4$ is derived from ring A, $1:5:6:2\text{-C}_{10}\text{H}_4\text{Me}_3\text{OH}$ from A and B, $1:2:5:6\text{-C}_{10}\text{H}_4\text{Me}_4$ from A and B after wandering of *Me* during elimination of H_2O , $2:7\text{-C}_{10}\text{H}_6\text{Me}_2$ and $1:2:7\text{-C}_{10}\text{H}_5\text{Me}_3$ from D and E, and $1:7:8\text{-trimethylphenanthrene}$ from A—C. Of the incompletely identified products $\text{C}_{18}\text{H}_{18}$, m.p. $126\text{--}127^\circ$, is possibly $1:2:7:8\text{-tetramethylphenanthrene}$ from rings A, B, C, and ?. The hydrocarbon, m.p. 245° , also obtained from hederagenin is probably $1:2:7:8\text{-tetramethylchrysene}$ from A, B, C, D. Synthetic comparison shows that the polymethylpicene is not identical with $1:2:10\text{-trimethyl-}$ or $1:10\text{-dimethyl-}$ picene; it is probably $1:2:8\text{-trimethyl-}$ or $1:8\text{-dimethyl-}$ picene or a mixture of these substances. Dehydrogenation of amyrin gives a *hydroxypicene*, $\text{C}_{24}\text{H}_{18}\text{O}$, m.p. $330\text{--}331^\circ$, the *Me* ether, m.p. $358\text{--}359^\circ$, of which is

provisionally regarded as $2\text{-methoxy-1:8-dimethylpicene}$. Very significant for the constitution is the



conversion of (*I*) into the acetyl-lactonedicarboxylic acid, to which structure (*II*) is assigned; this readily explains its dehydrogenation to $2:7\text{-C}_{10}\text{H}_6\text{Me}_2$. The previous location of the double linking in ring E was due to the observation of Schicke and Wedekind (A., 1933, 612) that acetyloleanolic acid is oxidised to "acetylviscolic acid" with loss of 5 C; repetition of this work shows that the sole acidic product is (*II*). (*I*) in rings A—C contains an ordered chain of four isoprene residues such as is present in most diterpenes whereas the remaining two residues which constitute rings D and E are irregularly arranged. H. W.

Constituents of natural phenolic resins. VIII. Lariciresinol, cubebin, and some stereochemical relationships. R. D. HAWORTH and W. KELLY (J.C.S., 1937, 384—391).—Lariciresinol (*I*), $\text{C}_{20}\text{H}_{24}\text{O}_6$, m.p. $167\text{--}168^\circ$, $[\alpha]_D^{25} +19.7^\circ$ in COMe_2 , forms a *Me*, ether, m.p. $79\text{--}80^\circ$, a *Et*, ether, m.p. $103\text{--}104^\circ$, and is readily isomerised by dil. acids to isolariciresinol



(*II*), m.p. 112° , $[\alpha]_D^{25} +69.4^\circ$ in COMe_2 [*Me* ether, m.p. $134\text{--}135^\circ$; *Ac*, derivative, m.p. 162° ; *Me*, ether

(+H₂O), m.p. 166—167°; *Et*₂ ether, m.p. 168°, and its *Ac*₂ derivative, m.p. 114—115°, $[\alpha]_D^{25} +21.7^\circ$ in *COMe*₂. (I) with *MeOH-HCl* yields *anhydrosolaric-resinol*, m.p. 209—210°, $[\alpha]_D^{25} +7.9^\circ$ in *AcOH* (*Me*₂ ether, m.p. 146—147°, $[\alpha]_D^{25} -33.4^\circ$ in *COMe*₂; *Et*₂ ether, m.p. 132—133°). Oxidation (*KMnO*₄) of the *Me*₂ and *Et*₂ ethers of (I) and also of the *Me*₂ and *Et*₂ ethers of (II) affords respectively veratric and 3-methoxy-4-ethoxybenzoic acids, and 2-veratrolylveratric and 5-methoxy-4-ethoxy-2-(3'-methoxy-4'-ethoxybenzoyl)benzoic acids. Conversion of (I) into (II) involves cyclisation of a diarylbutane into a 1-C₁₀H₇Ph derivative. Oxidation (*NaOBr*) of the *Me*₂ ether of (II) gives *l*-conidendrin *Me*₂ ether, identified by dehydrogenation to the lactone of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid. These results are in agreement with the structures assigned. Cubebin, m.p. 132°, $[\alpha]_D^{25} -17.1^\circ$ in *COMe*₂ (*semicarbazone*, m.p. 144°), is (III). It is suggested that matairesinol, hinokinin, arctigenin, olivil, and 1-phenylnaphthalene derivatives, *e.g.*, conidendrin, have a *trans*-configuration, whilst (I) and pinoresinol are *cis*-isomerides. F. R. S.

Constitution of soloric acid. G. KOLLER and H. RUSS (*Monatsh.*, 1937, 70, 54—72).—Extraction of the thalli of *Solorina crocea*, L., with *Et*₂O and crystallisation of the product from C₆H₆ followed by sublimation in a high vac. gives soloric acid (I), m.p. 203.5° (vac.), $[\alpha] \pm 0^\circ$, which is uniform according to chromatographic analysis (*Al*₂O₃). It contains 1 OMe. (I) is transformed by *Ac*₂O containing conc. *H*₂SO₄ at 100° into the *triacetate*, m.p. 147°, hydrolysed by *KOH-MeOH* to (I), and by *Me*₂SO₄-*KOH* into the *Me*₃ ether, m.p. 130.5° (vac.), and therefore contains 3 OH. Distillation of (I) with Zn dust affords 2-methylantracene. (I) with Zn dust and boiling *AcOH* affords the corresponding *anthranol*, C₂₁H₂₂O₆, m.p. 173° (vac.), oxidised by air in alkaline solution to (I). (I) with *NH*₂OH in boiling *EtOH* yields *soloric acid oxime*, m.p. 223° (vac.; decomp.); the behaviour of other tetrahydroxyanthraquinones shows that the quinone grouping remains intact under these conditions. Treatment of (I) with *PhOH* and *HI* (*d* 1.7) at 150° affords *MeI*, *n*-hexoic acid (II), and 1:3:6:8-tetrahydroxyanthraquinone (III), m.p. 334° [*tetra-acetate*, m.p. 196° (vac.; decomp.); *Me*₄ derivative, m.p. 241—242°]. (III) is transformed into anthracene by distillation with Zn dust and into a compound, C₁₄H₈O₆, m.p. >360°, by atm. oxidation. Drastic oxidation of (I) by *KMnO*₄ gives (II), whilst milder treatment appears to yield a little *MeCHO*. Hydrogenation (*Pd-C* in *AcOH*) of (I) gives probably a *methoxyhexatetradecahydroanthracene* (IV), m.p. 166° after softening at 165°, an *isomeride*, b.p. 125—132°/0.001 mm., and possibly a *hexylperhydroanthracene* (V), C₂₀H₃₆, b.p. 99—116°/0.001 mm. Analogous treatment of 1:4:5:8-tetrahydroxyanthraquinone shows that the ring is affected since the compound, C₁₄H₁₈O₃, m.p. 168°, is produced. Dehydrogenation of perhydroanthracene by *Se* at 260—290° gives anthracene but analogous treatment of (IV) and (V) gives ill-defined results. (I) is therefore 1:3:8-*tri-hydroxy-6-methoxy-2-n-hexoylanthraquinone*. H. W.

I (A., II.)

Bitter principles of Colombo root. V. Methylation of columbin. F. WESSELY and K. JENTZSCH (*Monatsh.*, 1937, 70, 30—36; cf. A., 1936, 1515).—Treatment of columbin (I) or *isocolumbin* (II) with *Me*₂SO₄ and *NaOH* affords *methylcolumbin* (III), C₂₁H₂₄O₆, m.p. 225° (decomp.), $[\alpha]_D^{25} +64.52^\circ$ in C₅H₅N, in which the function of the O is similar to that in (I) or (II) except as concerns OMe. The action of alkali on (III) depends largely on conditions and, under drastic conditions, leads to unchanged (III), a substance, m.p. about 290—300°, and a dibasic acid, C₂₁H₂₆O₇, decomp. 210° (*Me*₂ ester, m.p. 119.5° after softening at 116.5°). At 190—210° (III) yields CO₂ and *methyldecarboxycolumbin* (IV), C₂₀H₂₄O₄, m.p. 205—204°, $[\alpha]_D^{25} -383.7^\circ$ in anhyd. C₅H₅N, which cannot be obtained by methylation of decarboxycolumbin or *isocolumbin* (V). (IV) reacts with the amount of *NaOH* required for one lactone group and the solution when acidified yields (V). This unusual hydrolysis of OMe is not observed when (III) is treated similarly. H. W.

Sapogenins. II. Sarsasapogenin and smilagenin. S. N. FARMER and G. A. R. KON (*J.C.S.*, 1937, 414—420).—Sarsasapogenin (I) forms a *Me* ether, m.p. 153—155°, and its *Ac* derivative is oxidised (*H*₂CrO₄) to the *acetate* of a lactone (II), C₂₄H₃₈O₄, m.p. 184—185°, $[\alpha]_D^{25} -32^\circ$ in CHCl₃ (also obtained by oxidation of smilagenin *acetate*), a *lactone*, C₂₀H₃₀O₄, m.p. 220°, and a *Me* ester, C₃₀H₄₄O₁₁, m.p. 199—200°. (II) with *HBr* affords a *lactone*, C₂₄H₃₄O₃, m.p. 201°, and a *lactone*, C₂₂H₃₂O₂, m.p. 99°. Hydrolysis (*KOH-EtOH*) of (II) yields the *OH-lactone*, C₂₂H₃₄O₃, m.p. 202°, $[\alpha]_D^{25} -36.2^\circ$ in CHCl₃, oxidised (*H*₂CrO₄) to a *keto-lactone*, m.p. 184.5°, which is reduced (Clemmensen) to a deoxy-lactone, m.p. 133.5° (cf. Jacobs *et al.*, A., 1935, 1130). The deoxylactone with *MgPhBr* gives a *diphenylcarbinol* (+*COMe*₂), m.p. 205.5°, oxidised (*H*₂CrO₄) to an acid, C₃₇H₄₂O₂, m.p. 212—213°, and *ætiobiliaric* acid. Dehydration with *SOCl*₂-C₅H₅N of 3-methylcholestan-3-ol, m.p. 147°, from β-cholestanone, gives 3-methyl-Δ^{3(m)}-cholestene, m.p. 81—82°, but dehydration with *Se* yields 3-methylcholestane, m.p. 96—97°, or under different conditions a *dimethylcyclopentenophenanthrene*, m.p. about 165° [*s*-C₆H₃(NO₂)₃ complex (III), m.p. 165°]. A sample of a hydrocarbon prepared by *Se* dehydrogenation affords a C₆H₃(NO₂)₃ complex, m.p. 174—175°, from which an impure hydrocarbon, a methylcyclopentenophenanthrene, regenerated forms a *picrate*, m.p. 145—146°, *s*-C₆H₃(NO₂)₃ compound, m.p. 181—182°, and *styphnate*, m.p. 175—176°. Sarsasapogenone with *MgMeI* gives *methylsarsasapogenin*, m.p. 185°, dehydrogenated to an impure hydrocarbon, C₁₉H₁₆, m.p. 215—216° (?), the *s*-C₆H₃(NO₂)₃ complex of which is identical with (III); a portion of the hydrocarbon yields a *s*-C₆H₃(NO₂)₃ complex, m.p. 161—163°. (I) belongs to the coprostane series and the side chain is attached to ring IV at C₁₇ and one of the oxide rings to C₁₀. F. R. S.

Glycyrrhetic acid. E. BERGMANN and F. BERGMANN (*Helv. Chim. Acta*, 1937, 20, 207—208; cf. Ruzicka *et al.*, this vol., 202).—The isolation of a trimethylpicene, C₂₅H₂₀, from the products of the dehydrogenation of glycyrrhetic acid excludes the

possibility of the author's formula $C_{23}H_{36}O_5$. Treatment of $(NH_4)_2$ glycyrrhizate with NaOH and Me_2SO_4 gives the *Me H* ester, decomp. $263-264^\circ$, whereas the *Me_2* ester, decomp. 267° , is obtained by use of CH_2N_2 . H. W.

Resin alcohol, $C_{25}H_{41}O_2 \cdot OH$, + $0.5EtOH$, m.p. 272.5° (acetate, m.p. 188.5°), from *Periploca aphylla*.—See A., III, 191.

Eloxanthin, a new carotenoid pigment from the pondweed *Elodea canadensis*. D. HEY (Biochem. J., 1937, 31, 532-534).—Eloxanthin, $C_{40}H_{56}O_3$, m.p. $182.5-183^\circ$, $[\alpha]_D^{25} + 225^\circ$ in C_6H_6 , from the leaves of *E. canadensis*, contains 3 active H atoms (Zerevitinov) and 11 double linkings of which 9 are in conjugation (suggested by absorption data) and is isomeric with flavoxanthin but gives no colour reaction with 25% HCl. It is accompanied with carotene but lutein could not be detected. P. W. C.

Limonic, the bitter principle of orange kernels. II. G. KOLLER and H. CZERNY (Monatsh., 1937, 70, 26-29; cf. A., 1936, 857).—Limonic (I) has m.p. 280° , $[\alpha]_D^{20} -142.85^\circ$ in CH_2Cl_2 . Fresh determinations of the mol. wt. of hexahydrolimonic acid are recorded. (I) is very probably identical with Feist's citrolimonic (A., 1936, 995). H. W.

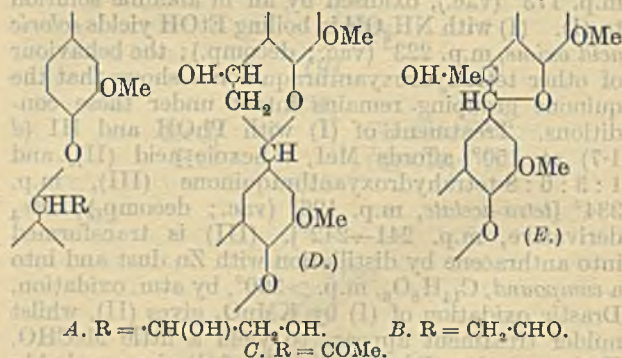
Constitution of ammosesinol. H. RAUDNITZ, K. LANNER, and E. DEUTSCHBERGER (Ber., 1937, 70, [B], 463-465; cf. A., 1936, 1259).—Repetition of the work of Späth (A., 1936, 1119) on the dissolution of diacetylhexahydroammosesinol (I) in warm 5% KOH and its subsequent oxidation with $KMnO_4$ ($= 9 O$) at room temp. shows the product to be $\gamma\gamma\lambda$ -trimethyl-*n*-tridecoic acid, b.p. $140^\circ/0.15$ mm. (*Me* ester, m.p. $120-125^\circ/0.15$ mm.; *p*-bromophenacyl ester, m.p. about 25°). (I) gives a distinct yellow colour with $C(NO_2)_4$ in $CHCl_3$ and hence does not contain a latent double linking. H. W.

Occurrence of acetone and syringic aldehyde as degradation products of lignin substances. A. BELL, W. L. HAWKINS, G. F. WRIGHT, and H. HIBBERT (J. Amer. Chem. Soc., 1937, 59, 598).—Stepwise oxidation or ozonolysis of HCO_2H -spruce lignin gives $COMe_2$, whilst alkaline fission of sulphite liquor from yellow birch wood affords syringic aldehyde. H. B.

"Cuproxam" lignins. Action of Schweitzer's reagent on wood and other components of plants. R. S. HILPERT and Q. S. WOO (Ber., 1937, 70, [B], 413-421).—Prolonged treatment of pine wood with Schweitzer's reagent (I) dissolves about 80% of the material. The residue contains 8% OMe and 1.8% N which is so firmly retained that it is not removed by boiling 1% H_2SO_4 although 24% of the substance is dissolved; treatment of it with 72% H_2SO_4 leaves 47% of material with 15% OMe and 1.7% N. It is impossible by this method to obtain a N-free substance. Reaction between wood and NH_3 occurs in absence of Cu compounds but only about 0.5% of N is retained in the product. The dissolved portion is not homogeneous cellulose (II) since it is incompletely pptd. by acids and the ppt. contains 2.1-2.6% OMe and N. White beech behaves similarly. When treated with (I), straw, jute, and sisal leave only

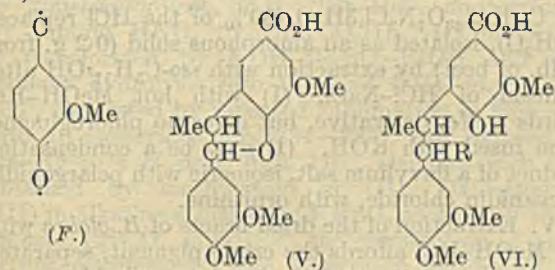
a small residue which contains an increased % of C and OMe and about 1% of N or 2.2% in the case of straw. Asparagus fibre (III) is largely dissolved and the residue is richer in C and H but not in N; the first ppt. contains 9% N, but this may be due to a component, rich in N, of the original material since the composition of the subsequent ppts. is similar to that from straw and jute. The product of the action of $NaHSO_3$ on (II) is almost completely sol. in (I) and the undissolved portion differs in C and H content from (II) or lignin. The dissolved material is closely similar to (II) and contains very little N. The product (IV) obtained from (III) and $NaHSO_3$ when treated with (I) leaves a residue richer in C and H than any product similarly prepared; the material pptd. by acid has the same C-H content as (IV) but the N content is increased from 0.27% to 1.12%. Union with N under the influence of (I) is a general phenomenon of the treatment of all parts of plants. The N content of the insol. product usually increases with the C content. The precipitable product has the composition of (II) only when this is possessed by the initial product (V); otherwise the composition lies between those of (II) and (V). It cannot therefore be assumed that (II) is present in the free form in the greater part of the skeleton matter of plants. The bearing of the experiments on the genesis of coal is discussed. H. W.

Lignin. XVI. Pinelignin. K. FREUDENBERG, M. MEISTER, and E. FLICKINGER (Ber., 1937, 70, [B], 500-514).—Lignin (I) is composed of simple units united by etherification. The side-chain of the unit consists of the biologically equiv. forms, $OH \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot$, $CHO \cdot CH_2 \cdot CH(OH) \cdot$, or $COMe \cdot CH(OH) \cdot$, and the nucleus is of the type of vanillin, piperonyl, or, possibly, isovanillin. The assumption that etherification is concerned only with the primary OH is unnecessary and uniformity is secured in the sense, A—C. The physiological or



post-mortem condensation to D or E is thus readily explained. From the % CH_2O obtained from (I) it appears that (I) is composed of about 7 units in etheral linking according to A, B, and C and probably exists thus in the primary lignin of young wood. Condensation according to D or E takes place in the wood and, postmortally or under the influence of chemical reagents, condensation of CO of B and C with terminal CO of D or E occurs with production of three-dimensional products of high mol. wt. Moderated treatment of (I) with alkali followed by methyl-

ation and oxidation gives veratric (II) (10%), isohemipinic (III) (3%), and 2:3:2':3'-tetramethoxydiphenyl-5:5'-dicarboxylic acid (IV). It is uncertain whether (IV) exists pre-formed in (I) or is formed during the degradation. (III) does not appear to be derived from (IV). Degradation, ethylation, and oxidation of (I) affords 3-methoxy-4-ethoxybenzoic acid in 10% yield. Protocatechuic acid and (II) are therefore derived from the arrangement *F*. Lignin-sulphonic acid, purified through the quinoline salt and by electrodialysis, when methylated and oxidised gives 1–2% of (II) and nearly 1% of (III). Lignin-thiolacetic acid does not give aromatic acids when oxidised. When methylated and then oxidised it yields 4% of (II) and 3% of (III); (IV) is not produced. As model experiment for the production of (III) from *D* or *E* the behaviour of Erdtman's acid



(V) has been investigated. When oxidised it gives exclusively (II) in 32% yield (calc. 53%). When treated successively with alkali and CH_2N_2 and then oxidised it yields 21% of (II) and 5% of (III). (V) is converted by SO_3 into the non-cryst. sulphonic acid (VI; $\text{R} = \text{SO}_3\text{H}$); the non-cryst. *Me* ester is oxidised to 17% of (II) and 4% of (III), thus closely resembling methylated ligninsulphonic acid. (V) and $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ yield a product containing the analogue (VI; $\text{R} = \text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$) which when methylated, hydrolysed, and then oxidised affords 7.4% of (II) and 3% of (III). Holmberg's model experiments with $\text{CHPhMe}\cdot\text{OH}$ and $\text{CHPh}_2\cdot\text{OH}$ and $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ are discussed. The actions of alkali, SO_3 , and $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ on (I) are reviewed. H. W.

Alkaline degradation of pine wood. II. R. S. HILPERT and O. PETERS (Ber., 1937, 70, [B], 514–517).—Successive treatments of pinewood with $\text{NaOH}\cdot\text{H}_2\text{O}$ and CH_2PhCl give a CH_2Ph derivative which very closely resembles benzylcellulose and is extensively sol. in conc. HCl . The presence of benzyl-lignin is not detectable. Lignin obtained from wood by acids is therefore a reaction product and not a component thereof. Pine wood is converted by NaOH followed by CS_2 into a xanthate which is completely sol. in H_2O . Addition of acid to the solution ppts. a material (yield 50%) with 4.7% OMe and the composition of a cellulose anhydride, $2\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{H}_2\text{O}$. The sol. portion appears further degraded. Cellulose is obtained from the xanthate only when used as initial material. Free cellulose is not present in the wood. H. W.

Mercuriation of wood, straw, and lignin. Evidence against the presence of aromatic components. R. S. HILPERT, E. LITTMANN, and R. WEINBECK (Ber., 1937, 70, [B], 560–567).—Distinction between mercuriation at a double linking and

in the C_6H_6 nucleus is effected by treating the products with $(\text{NH}_4)_2\text{S}$ whereby, in the former case, HgS is pptd. usually immediately but sometimes gradually, whereas in the latter case the products are stable provided that only one residue has entered the nucleus. Hot, dil. mineral acid usually causes decomp. of the former but not of the latter class of compound. Vanillin is transformed by $\text{Hg}(\text{OAc})_2$ in AcOH into a product with about 1.5 atoms of Hg which is stable to prolonged heating with 5% HCl . Under similar conditions pine wood gives a material with 8% Hg which is completely removed by $(\text{NH}_4)_2\text{S}$ or dil. HCl . With boiling 1% AcOH , pine wood, rye straw, and wheat straw slowly yield products with 28–30% Hg which is readily removed. With raw and bleached cotton and cellulose there appears a relationship between the extent of mercuriation and the content of "apparent" lignin, but there is no evidence of nuclear substitution. The ability of Ph , even if chemically united in wood, to give typical Hg compounds is established by comparison of $\text{BuCO}_2\cdot\text{CH}_2\text{Ph}$, which yields a product containing 2 Hg part of which is removable by HCl leaving a stable residue, with benzylcellulose or benzyl-pine wood each of which gives a product with about 20% Hg which is not removed by $(\text{NH}_4)_2\text{S}$ or dil. HCl . Straw lignin and pine lignin in boiling 1% AcOH slowly give products with (max.) 43% Hg which can be removed with the exception of 4–6% Hg by dil. HCl . The substances obtained from fructose and xylose under the conditions of the lignin determination with H_2SO_4 behave analogously. The small residue of Hg can be attributed to aromatic components which must then be contained in the products derived from the sugars. According to behaviour on mercuriation, it is very improbable that wood and straw contain aromatic components. Addition appears to occur at a double linking, the character of which is not yet defined. The aromatic compounds from wood are therefore the products of chemical action. H. W.

Preparation of gliadin and zein.—See A., III, 191.

Velocity of reaction between furfuraldehyde and acetophenone.—See A., I, 249.

Synthesis of benzalfurfuralazine. S. A. TEBINOV (J. Gen. Chem. Russ., 1936, 6, 1902–1903).— PhCHO , furfuraldehyde, and N_2H_4 yield *NN'*-benzylidenefurfurylideneazine, m.p. 99–100°. R. T.

Preparation of substituted xanthenes and xanthhydrols. A. LESPAGNOL and J. DUPAS (Bull. Soc. chim., 1937, [v], 4, 541–548).—The standard methods of prep. of xanthenes give increasing amounts of "disalicyde," $\text{C}_6\text{H}_4\cdot\text{C}(\text{CO}_2\text{O})\cdot\text{C}_6\text{H}_4$, as the wt. of the substituents increases. The prep. of 4:5-dimethyl-, 1-methyl-4-isopropyl- (from *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, thymol, and Ac_2O), m.p. 169°, and 1:5-dimethyl-4-isopropyl-xanthone (from *m*-cresotic acid, thymol, and Ac_2O), m.p. 165° (with 75–80% of "di-*o*-cresotide," m.p. 234°), is detailed. 1:8-Dimethyl-4:5-diisopropylxanthone could not be obtained from thymotic acid, only "di-*o*-thymotide," m.p. 212°, being formed. $\text{Zn}\cdot\text{NaOH}\cdot\text{EtOH}$ gives

the corresponding xanthhydrols. 2:7-Dibromoxanthone (prep. erratic) could not be reduced without elimination of Br. R. S. C.

Reactions of *o*-hydroxybenzylideneacetophenones. VII. Flavylium salts from dihydrochalcones. A. D. HARFORD and D. W. HILL (J.C.S., 1937, 41—42).—4-Methoxy-, m.p. 64—65° (phenylhydrazone, m.p. 140—141°; O-Ac derivative, m.p. 84—85°), and 3':4-dimethoxy-, m.p. 89—90° (phenylhydrazone, m.p. 145—146°; O-Ac-derivative, m.p. 55—56°), -*o*-salicylaceto-phenone, obtained by reduction (H_2 -Pt) of the appropriate salicylideneacetophenone, and *o*-salicylaceto-phenone (O-Ac derivative, m.p. 65°), when treated with $FeCl_3$ -HCl-AcOH yield, respectively, without the aid of an oxidising agent, the corresponding flavylium ferri- chlorides. The salicylaceto-phenones are unaffected by HCl-EtOH and when refluxed with AcOH, but were acetylated by Ac_2O (cf. salicylacetone, A., 1935, 985).

H. G. M.

Constitution of tannins. V. Synthesis of some flavpinacols. A. RUSSELL and J. TODD (J.C.S., 1937, 421—424).—*o*-Benzoyloxyacetophenone and vanillin benzoate with HCl give 2:4'-dibenzoyl-3'-methoxychalcone, m.p. 118—119°, hydrolysed to the 2:4'-dihydroxy-compound, m.p. 128°, which with Zn-HCl yields bis-(4'-hydroxy-3'-methoxy)flavpinacol. Similar reactions with the appropriate reagents lead to 2:4:4'-tribenzoyloxy-, m.p. 148°, and 2:4:4'-trihydroxy-3'-methoxychalcone, m.p. 210°, bis-(7:4'-dihydroxy-3'-methoxy)flavpinacol; 2:4:6:4'-tetrahydroxy-3'-methoxychalcone, m.p. 214° (Bz_4 derivative), bis-(5:7:4'-trihydroxy-3'-methoxy)flavpinacol; 2:3:4:4'-tetrahydroxy-3'-methoxychalcone, m.p. 199—200° (Bz_4 derivative, m.p. 95°), bis-(7:8:4'-trihydroxy-3'-methoxy)flavpinacol; 2:4'-dihydroxychalcone, m.p. 145° (Bz_2 derivative, m.p. 120°), bis-(4'-hydroxy)flavpinacol; 2:4:4'-trihydroxychalcone, m.p. 187—188° (Bz_2 derivative, m.p. 114—115°), bis-(7:4'-dihydroxy)flavpinacol; 2:3:4:4'-tetrahydroxychalcone, m.p. 117° (Bz_4 derivative, m.p. 105°), bis-(7:8:4'-trihydroxy)flavpinacol; 2:4:6:4'-tetrahydroxychalcone, m.p. 205° (Bz_4 derivative), and bis-(5:7:4'-trihydroxy)flavpinacol. Derivatives of the parent flavpinacol bearing free OH have been compared with others in which the 3'-OH has been eliminated or replaced by OMe. The two latter series of flavpinacols are not directly comparable with natural phlobatannins, but the properties of the first group show that free OH in the 3':4' positions suffice for the reproduction of full tanning properties in a substance of this type. 2:4:6:3':4'-Pentahydroxy- and 2:4:6:4'-tetrahydroxy-3'-methoxychalcone have been prepared and converted into the corresponding flavanones, which have been shown to be identical with eriodictyol and homoeriodictyol, respectively.

F. R. S.

Constitution of fustin. V. Synthesis of 3-hydroxy-4'-methoxyflavanone. T. OYAMADA (J. Chem. Soc. Japan, 1935, 56, 980—983).—Synthetic 3-hydroxy-4'-methoxyflavanone is identical with methylfustin.

CH. ABS. (r)

Colouring matters of Grimes Golden, Jonathan, and Stayman Winesap apples. C. E.

SANDO (J. Biol. Chem., 1937, 117, 45—56).—3-Galactosidylquercetin, m.p. 236.5—237.5°, hydrolysed to *d*-galactose and quercetin, and, after methylation, to 3-hydroxy-5:7:3':4'-tetramethoxyflavone, has been isolated from the skins of Grimes Golden and Jonathan apples, and idaein (3- β -galactosidylcyanidin) from Jonathan and Stayman Winesap apples.

H. G. M.

Nitrogenous anthocyanins. III. Preliminary experiments with betanidin. A. D. AINLEY and R. ROBINSON. IV. Colouring matter of *Bougainvillea glabra*. J. R. PRICE and R. ROBINSON. V. Synthesis of substituted amino-flavylium salts. A. D. AINLEY and R. ROBINSON (J.C.S., 1937, 446—449, 449—453, 453—456).—III. Aq. extracts of beet undergo fermentation when kept (9—11 days), liberating betanidin chloride (I), $C_{20}H_{19-23}O_7N_2Cl \cdot 3H_2O$ (30% of the HCl replaced by H_2O), isolated as an amorphous solid (0.2 g. from 56 lb. of beet) by extraction with $iso-C_5H_{11} \cdot OH$ after addition of HCl-NaCl. (I) with hot MeOH-HCl affords a Me_2 derivative, but gives no phloroglucinol when fused with KOH. (I) may be a condensation product of a flavylium salt, isomeric with pelargonidin or cyanidin chloride, with ornithine.

IV. Extraction of the dried bracts of *B. glabra* with 1% MeOH-HCl affords the crude pigment, separated by subsequent treatment involving shaking with saturated brine-BuOH-conc. HCl and chromatographic adsorption on Al_2O_3 into a glucosidic portion, quercetin, and bougainvillaidin chloride (absorption spectrum in the visible region is plotted; distribution no. between $n-C_5H_{11} \cdot OH$ -0.5% HCl = 50). Analytical data suggest that the isolated anthocyanidin is a mixture of approx. 2 parts of bougainvillaidin (betaine), $C_{22}H_{23}O_8N \cdot 2H_2O$, and 1 part of its Me ester chloride, $C_{22}H_{26}O_8NCl \cdot 2H_2O$.

V. $CH_2Br \cdot CO_2Et$ -NaI in $COMe_2$ with $p-NH_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot OAc$ give 4-carbethoxymethylamino-*o*-acetoxyacetophenone, m.p. 113°, which condenses with β -resorcylaldehyde in dry dioxan-HCl and with 2-*O*-benzoylphloroglucinaldehyde in EtOAc-HCl at 0° to give, respectively, 4-carbethoxymethylamino-3:7-dihydroxyflavylium chloride and its 5-*OBz*-derivative: a similar chloride is obtained from *o*-vanillin. $s-C_6H_3(OH)_3$ and $NH_2 \cdot CH_2 \cdot CO_2Et$ in EtOH (N_2) afford Et 3:5-dihydroxyamilinoacetate, m.p. 153.5—154°, which with chloranil-EtOH-HCl and OH·CBz·CH₃ or OH·CBz·CHPh gives, respectively, 5-(or 7)-carbethoxymethylamino-3:7-(or 3:5)-dihydroxyflavylium chloride + $3H_2O$, and its 4-*Ph* derivative + $2.5H_2O$. The following were prepared in connexion with abandoned syntheses: Et 4-carbethoxymethylaminoacetate, m.p. 63—63.5° (from the acid); *o*-chloro-4-*p*-toluenesulphonamido-, m.p. 184°, and 4-*p*-toluenesulphonamido-*o*-acetoxyacetophenone, m.p. 179—179.5° (from the NH_2 -compound and $p-C_6H_4Me \cdot SO_2Cl$), which with $CH_2Br \cdot CO_2Et$ -Et₂O-aq. NaOH affords the *o*-hydroxyacetophenone, m.p. 202—204° (decomp.); *p*-acetoxypropionophenone, m.p. 59°, from the OH-compound and Ac_2O .

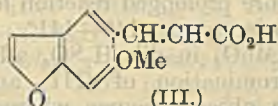
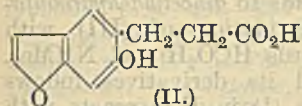
J. W. B.

Natural coumarins. XXIV. Synthesis of bergapten. E. SPÄTH, F. WESSELY, and G. KUBICEK (Ber., 1937, 70, [B], 478—479).—The product

obtained by successive treatments of 3:4:6-triacet-oxy-coumarin with Et sodioformylacetate and CH_2N_2 is separated into *allobergapten* and *bergapten*, m.p. 188—190°.

H. W.

Derivatives of psoralene. H. S. JOIS and B. L. MANJUNATH (Ber., 1937, 70, [B], 434—438).—Psoralene (I) is converted by HNO_3 (d 1.52) in cold AcOH into *nitropsoralene*, m.p. 278—279° (decomp.),



in small yield. Treatment of (I) with dil. NaOH followed by reduction with Na-Hg affords the *acid* (II), m.p. 133—134°, readily lactonised at 155°/vac. to *dihydropsoresalene*, m.p. 105—106°, and oxidised by fuming HNO_3 to $(\text{CH}_2\text{CO}_2\text{H})_2$. (I) in COMe_2 is transformed by $\text{KOH-Me}_2\text{SO}_4\text{-EtOH}$ and subsequent hydrolysis into the *acid* (III), m.p. 163—166°, converted by repeated sublimation in high vac. into an *isomeride*, m.p. 234—235°, and reduced by Na-Hg to a *H₂-acid*, m.p. 116°, identical with that obtained by methylation of (II). Oxidation of (III) in alkaline solution by KMnO_4 at 40—50° yields an *acid*, $\text{C}_9\text{H}_8\text{O}_4$, m.p. 182°, the constitution of which is not established. The absorption spectra of (I), *isopsoralene*, *pimpinellin*, *isopimpinellin*, and *isobergapten* are recorded.

H. W.

Reactivity of chlorine in 1:1-dioxy-3-chloro-4-methyl- Δ^3 -thiacyclopentene. H. J. BACKER and S. VAN DER BAAN (Rec. trav. chim., 1937, 56, 181—185).— β -Chloro- γ -methylbutadiene and SO_2 in Et_2O afford 3-chloro-4-methyl- Δ^3 -thiacyclopentene 1:1-dioxide (I), m.p. 145—147° (decomp.), converted by NaSMc in EtOH into 4-methylthiol-3-methyl- Δ^3 -thiacyclopentene 1:1-dioxide, m.p. 101°, which is oxidised ($\text{H}_2\text{O}_2\text{-AcOH}$) to 4-methylsulphonyl-3-methyl- Δ^3 -thiacyclopentene 1:1-dioxide, m.p. 192.5° (decomp.), and by NaSBu^v to 4-tert.-butylthiol-3-methyl- Δ^3 -thiacyclopentene 1:1-dioxide, m.p. 74—75°, oxidised to 4-tert.-butylsulphonyl-3-methyl- Δ^3 -thiacyclopentene 1:1-dioxide, m.p. 193° (decomp.). With K_2S in EtOH (I) affords 4:4'-bis-(3-methyl- Δ^3 -thiacyclopentene 1:1-dioxide) sulphide, m.p. 163—164°, oxidised to the sulphone, m.p. 192°; $\text{H}_2\text{-Pt}$ in AcOH reduce (I) to 3-methylthiacyclopentane 1:1-dioxide, b.p. 100—102°/2 mm., m.p. 0—1°.

J. D. R.

Tetramethylmethanetetrasulphonic acid. H. J. BACKER and N. EVENHUIS (Rec. trav. chim., 1937, 56, 174—180).— Na_2S_4 and $\text{C}(\text{CH}_2\text{Br})_4$ in EtOH afford 2:3:7:8-tetrathia-5-spiro-nonane 2:7-disulphide (I), m.p. 182—184°, converted by Na or Cu in boiling PhMe into 2:3:7:8-tetrathia-5-spiro-nonane (II), m.p. 80—80.5° (HgCl_2 compound, m.p. 132°), and by K_2S into 2:3:7:8-tetrathia-5-spiro-nonane 2-sulphide, m.p. 117.5—118°. (I) or (II) with $\text{H}_2\text{O}_2\text{-AcOH}$ affords tetramethylmethanetetrasulphonic acid [tetrachloride, by PCl_5 ; Na salt, m.p. 217° (decomp.)].

J. D. R.

Configuration of heterocyclic compounds. V. Thianthren and phenoxthionine derivatives. G. M. BENNETT, M. S. LESSLIE, and E. E. TURNER

(J.C.S., 1937, 444—446).—Thianthren with NPhEt-COCl-ZnCl_2 at 160—170° and hydrolysis with aq. EtOH-NaOH gives thianthren-2(?)-carboxylic acid (I), m.p. 224° (amide, m.p. 227°; anilide, m.p. 200—201°; 1- α -phenylethylamine salt, m.p. 286—288°, $[\alpha]_{5461} -3.8^\circ$ in MeOH). 3-Thiol-*p*-tolyl carbonate (improved prep.) in boiling aq. EtOH-KOH with 2:3:5- $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2\text{-CO}_2\text{H-KOH}$ gives 3-nitro-8-methylphenoxthionine-1-carboxylic acid (II), m.p. 253—254° (brucine salt, $[\alpha]_{5791} -3.4^\circ$ in CHCl_3). Phenoxthionine (improved prep.) with NPhEt-COCl-ZnCl_2 at 190—200° affords its 2-(or 1-)carboxylic acid (III), m.p. 230—238° (strychnine, m.p. 178—179°, $[\alpha]_{5461} -10.9^\circ$ in CHCl_3 , and 1- α -phenylethylamine, m.p. 188—189°, $[\alpha]_{5791} -3.25^\circ$ to -4.6° in MeOH, salts). No resolution of (I), (II), or (III) could be effected.

J. W. B.

Exchange of hydrogen between pyrrole and water.—See A., I, 250.

Catalytic formation of heterocyclic compounds. G. G. SCHNEIDER, H. BOCK, and H. HAUSER (Ber., 1937, 70, [B], 425—429).—Passage of $\text{NH}_3 + \text{C}_2\text{H}_2$ over SiO_2 gel activated by $\text{Al}_2\text{O}_3\text{-CdO}$ (I), Al_2O_3 , or Fe_2O_3 at 400° and 480°, 420°, and 420°, respectively, affords pyrrole (II) in small yield. (II) in H_2 is decomposed by (I) at 430°, 510°, and 620° with formation of HCN and NH_3 whilst C_2H_2 and C_2H_4 could not be detected. The intermediate formation of a hydrocarbon with conjugated double linkings in the production of (II) is rendered probable by the better yield obtained when butadiene (III) and NH_3 are passed over Pt-asbestos, Cu, Ni, or (best) over (I); oxidising catalysts are not more effective. Further improvement in yield is observed when nascent NH_3 [(III) and NO] is employed. The catalytic action of C_2H_2 and NH_3 can result in the formation of (II) through a conjugated system, the production of $\text{C}_5\text{H}_5\text{N}$ through C_2H_2 and HCN, or the formation of derivatives of $\text{C}_5\text{H}_5\text{N}$ through aldehydeammonias. (III) and H_2S in presence of pyrites yield thiophen but not its homologues; reaction occurs at a higher temp. than that required by $\text{C}_2\text{H}_2 + \text{H}_2\text{S}$.

H. W.

Action of nitroprusside on pyrroles. G. SCAGLIARINI (Atti R. Accad. Lincei, 1936, 24, 294—299).—1-Phenyl-, 1-methyl-2:5-diethyl-, 5-carbethoxy-2-methyl-, 5-propionyl-2-methyl-4-ethyl-, and 2:3:5-trimethyl-4-ethyl-pyrrole, pyrrole-2-aldehyde, and 2:4-dimethylpyrrole-5-aldehyde do not react with nitroprusside, which with pyrrole, and 2:4-dimethyl- and 3-methyl-4-ethyl-pyrrole gives colorations, with 2:5-dimethylpyrrole yields a ppt., and with 2-methyl- and 2-acetyl-pyrrole forms the compounds $\text{K}_4[\text{Fe}(\text{CN})_5\text{-NO:C}_4\text{H}_2\text{N-Me}] \cdot 4\text{H}_2\text{O}$ and $\text{K}_4[\text{Fe}(\text{CN})_5\text{-NO:C}_4\text{H}_2\text{N-Ac}] \cdot 2\text{H}_2\text{O}$.

E. W. W.

Preparation of acetothranil derivatives. M. HAYASHI, I. MORIKAWA, and H. NAMIKAWA (J. Chem. Soc. Japan, 1935, 56, 1102—1105).—Preps. of a no. of anthranil derivatives are described.

CH. ABS. (7)

Adrenaline and adrenochrome. D. E. GREEN and D. RICHTER (Biochem. J., 1937, 31, 596—616).—Malic acid is rapidly oxidised by a system comprising coenzyme, CN' , adrenaline (I), and heart muscle malic acid dehydrogenase. The initiation of the reaction

depends on the primary oxidation of (I) to a red pigment. A similar red pigment, *adrenochrome* (II), $C_9H_9O_3N$, m.p. 115–120° (decomp.) {*oxime*, m.p. 278°; *Br*- and *I*-derivatives; reduction product, *leucoadrenochrome* (III) $[\alpha]_D^{25} +79.2^\circ$ }, was isolated by the action of pyrocatechol oxidase on (I) and shown to be 3-hydroxy-*N*-methyl-2:3-dihydroindole-5:6-quinone. (II) is probably identical with the red compound formed in the malic dehydrogenase system in that it behaves equally well as O_2 carrier when added thereto and gives the same quant. results. Oxidising agents [cytochrome *C* (IV) and H_2O_2] accelerate and reducing agents (ascorbic acid and glutathione) retard its formation. The primary formation of (II) from (I) is probably effected by a h matin compound similar to (IV) shown spectroscopically to be present in the enzyme prep. In the absence of CN^- , (I) and (III) are readily oxidised by the indophenol-oxidase-cytochrome system. P. W. C.

Heterocyclic compounds containing nitrogen.
XXVII. Preparation of 2-phenylisatogen and 6-carbethoxy-2-phenylisatogen. P. RUGGLI, E. CASPAR, and B. HEGED S (Helv. Chim. Acta, 1937, 20, 250–263).—Decarboxylation of o - $NO_2 \cdot C_6H_4 \cdot CH : CPh \cdot CO_2H$ affords *cis*- o - $NO_2 \cdot C_6H_4 \cdot CH : CPh$ (I), isomerised when heated with I in $PhNO_2$ into *trans*- o - $NO_2 \cdot C_6H_4 \cdot CH : CPh$ (II). Chlorination of (I) gives *o*-nitrostilbene dichloride (III), m.p. 122°, whereas that of (II) gives the isomeride (IV), m.p. 77–79°. Treatment of (III) and (IV) with $NaOH$ - $EtOH$ affords *o*-nitrotolane (V) in 36% and 74–90% yield, respectively. Irradiation of (III) or (IV) by sunlight or artificial light leads so slowly to 2-phenylisatogen (VI) that the change is not practical although accompanied by little resinification. Reaction occurs still more slowly with (V). The best synthesis of (VI) is from (V) and $PhNO$ in $CHCl_3$ in the dark, change occurring slowly at room temp. A reaction mechanism is suggested. In attempts to prepare o - $NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2Ph$, o - $NO_2 \cdot C_6H_4 \cdot COCl$ is condensed with $CN \cdot CPh \cdot Na \cdot CO_2Et$ to *Et* cyano-*o*-nitrobenzoylphenylacetate, m.p. 118°, which regenerates the initial materials when hydrolysed by alkali and either suffers the same change slowly or is unaffected when treated with acids. Similarly o - $NO_2 \cdot C_6H_4 \cdot COCl$ and $CPhNa(CO_2Et)_2$ yield *Et*₂ *o*-nitrobenzoylphenylmalonate, m.p. 104°, which could not be satisfactorily hydrolysed. The best method for the prep. of 6-carbethoxy-2-phenylisatogen consists in converting 2-nitro-4-cyanostilbene dichloride by Na_2CO_3 in boiling $EtOH-H_2O$ into 2:4- $NO_2 \cdot C_6H_3(ON) \cdot CCl : CHPh$, which is slowly hydrolysed by boiling $HCl-EtOH$ to 4:2- $CO_2Et \cdot C_6H_3(NO_2) \cdot CCl : CHPh$; the latter substance is irradiated in C_5H_5N by a 300-watt Osram lamp. H. W.

Toad poisons. X. Constitution of bufothionin. H. WIELAND and T. WIELAND (Annalen, 1937, 528, 234–246).—Bufothionin (I), isolated from *Bufo arenarum*, is converted by dil. HCl into H_2SO_4 and dehydrobufotenin hydrochloride (II) (corresponding *picrate*, m.p. 186°), transformed by $TIOEt$ in abs. $EtOH$ into *dehydrobufotenin* (III), $C_{12}H_{14}ON_2$, m.p. 218° or (+1.5 H_2O) m.p. 199° (decomp.). Ex-

haustive treatment of (II) with MeI and $TIOEt$ in abs. $EtOH$ gives the *methiodide*, m.p. 208° (corresponding *picrate*, m.p. 103–104°), of the methoxylated base which is not hydrogenated (PtO_2 in H_2O) and is converted by KOH at 160°/high vac. into dehydrobufotenin Me ether in good yield. Short treatment of (II) with boiling Ac_2O appears to yield an *Ac*₁ derivative, m.p. 265° (decomp.), whereas more prolonged reaction leads to *diacetyldehydrobufotenin*, m.p. 140–141°. Oxidation of (III) with $KMnO_4$ in dil. H_2SO_4 affords HCO_2H and $NHMe_2$. Bromination of (III) and its derivatives follows an obscure course whereas (I) in H_2O reacts with exactly 4 Br and gives the compound, $C_{12}H_{13}ON_2BrSO_4$, m.p. 186.5° (decomp.), hydrolysed by CO_2-H_2O to the substance, $C_{12}H_{14}ON_2BrSO_4$, m.p. 171–172° (decomp.), which does not give the colour reactions of indole. Removal of H_2SO_4 is effected by $HCl-MeOH$ or 3*N*- HBr , thus leading to the *hydrochloride*, m.p. 241° (decomp.), and *hydrobromide*, m.p. 210–211° (decomp.), of 5-hydroxy-2-keto-3-dimethylamino-acetyl-2:3-dihydroindole, the constitution of which is established by its fission by alkali to β-keto-γ-dimethylamino-α-2-amino-5-hydroxyphenyl-*n*-butyric acid, m.p. 218° (decomp.), which can be diazotised and then coupled with β- $C_{10}H_7 \cdot OH$. Hydrogenation of (III) does not occur in basic or neutral solution whereas in an acid medium bufotenin (IV) is produced. (III) is therefore 5-hydroxy-3-β-dimethylaminovinylindole. (IV) gives a yellow monopicate (V), which at 140° passes into the red monopicate (VI), m.p. 178°. The red compound, m.p. 177–178°, of Hoshino and Shimodaira (A., 1935, 1378) is a *dipicrate* (VII). (VII) is converted into (V) when boiled with C_6H_6 and into (VI) when crystallised from H_2O containing $NaHCO_3$. H. W.

Reduction of the pyridine ring by formic acid. F. R. MAYO (J. Org. Chem., 1936, 1, 496–503).— C_5H_5N , HCO_2H , and $MeOH$ (or CH_2O), which at 100° give only traces of a quaternary salt, at 175–200° give up to 60% of 1:1-dimethylpiperidinium formate, m.p. 140–180° deliquescent (corresponding *chloride*, decomp. 330–340°). 1-Methylpyridinium formate and 1-methylpiperidine are intermediate products. 1-Methylpyridinium chloride and $HCO_2H-MeOH$ do not react until HCO_2K is added; with HCO_2K , but without $MeOH$, the yield is poor. E. W. W.

Action of nitrobenzoyl chlorides on pyridine. B. M. BOGOSLOVSKI (J. Gen. Chem. Russ., 1937, 7, 255–257).— C_5H_5N and *o*-, *m*-, and *p*- $NO_2 \cdot C_6H_4 \cdot COCl$ yield quinonoid additive products, m.p. 149–150°, 124–125°, and 228–230°, respectively, in which the N is tervalent, and Cl is substituted in position 2 or 4 of the quinonoid ring. R. T.

2:4-Diketo-3:3-dialkyltetrahydropyridines.—See B., 1937, 289.

Enol-betaines. III. Detection of reactive hydrogen atoms. F. KR HNKE and H. K BLER (Ber., 1937, 70, [B], 538–542; cf. A., 1936, 1510).—Further evidence of the presence of active H atoms in “methine-enol-betaines,” $R \cdot C \ddot{O} : CH \cdot \dot{N}^+$, is adduced. The enol-betaine from phenacylpyridinium bromide is

converted by PhNCO into (ω -phenylcarbamyphenacyl)-pyridinium enol-betaine, $\text{PhCO}:\text{C}(\text{CO}\cdot\text{NHPh})\cdot\text{NC}_5\text{H}_5$, decomp. $>210^\circ$, which gives a red-brown colour with FeCl_3 in EtOH and a negative reaction with chloranil and picryl chloride. It gives a bromide, $\text{COPh}\cdot\text{CH}(\text{CO}\cdot\text{NHPh})\cdot\text{N}(\text{C}_5\text{H}_5)\text{Br}$, m.p. $177\text{--}179^\circ$, perchlorate, m.p. $172\text{--}173^\circ$, and picrate, m.p. 174° . It is hydrolysed to N-phenylcarbamydimethylpyridinium bromide, m.p. $203\text{--}204^\circ$ after softening at 201° , also obtained from $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{NHPh}$ and $\text{C}_5\text{H}_5\text{N}$ in boiling EtOH. ω -Phenylcarbamy-p-bromophenacylpyridinium enol-betaine, m.p. 210° (decomp.), is converted by distillation/high vac. into $\text{C}_5\text{H}_5\text{N}$, PhNCO, and a substance, m.p. $231\text{--}234^\circ$; the perchlorate, m.p. about 160° , gives $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$ when crystallised from H_2O . ω -Phenylcarbamy-2:4:6-trimethylphenacylpyridinium enol-betaine, m.p. $210\text{--}211^\circ$ (decomp.) [bromide, m.p. $250\text{--}251^\circ$ (decomp.) after much darkening], is not hydrolysed by boiling N-NaOH or N-HBr. α -Naphthylcarbamyphenacylpyridinium enol-betaine has m.p. 211° (decomp.). ω -Phenylthiocarbamyphenacylpyridinium enol-betaine, decomp. 172° (perchlorate, m.p. 171°), gives PhNCS when heated at $180\text{--}190^\circ/0.6\text{ mm.}$; it is hydrolysed by 2N-HBr to BzOH and (with HClO_4) N-phenylthiocarbamydimethylpyridinium perchlorate, m.p. $200\text{--}201^\circ$ (decomp.). The active H of the methines is also detected by Zerevitinov's method. p -Bromophenacylpyridinium enol-betaine, PhN_2Br , and NaOH in EtOH readily afford ω -phenylhydrazino- p -bromophenacylpyridinium enol-betaine, m.p. $108\text{--}109^\circ$ (bromide, m.p. $219\text{--}220^\circ$). H. W.

Enol-betaines. IV. New type of enol-betaines. F. KRÖHNKE [with A. SCHULZE] (Ber., 1937, 70, [B], 543–547).—The possibility that the formation of enol-betaines from compounds, $\cdot\text{CO}\cdot[\text{CH}_2]_n\cdot\text{N}$ -cyclic residue, is general provided that CH_2 vicinal to CO contains a sufficiently labile H atom is not supported by the observation that propiophenonylpyridinium chloride is converted by cold NaOH or Na_2CO_3 or by warm H_2O into Ph vinyl ketone. Definite evidence of the production of an enol-betaine is not obtained when $\text{C}_5\text{H}_5\text{N}$ is replaced by NAlk_3 . $\text{C}_5\text{H}_5\text{N}$ and $\text{CHBr}(\text{CO}_2\text{Et})_2$ readily yield dicarbethoxymethylpyridinium perchlorate, m.p. 152° after softening, converted by K_2CO_3 into the enol-betaine ($\text{C}_5\text{H}_5\cdot\text{N}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{O})\cdot\text{OEt}$, m.p. $170\text{--}171^\circ$ (bromide, m.p. $70\text{--}71^\circ$ after softening). $\text{C}_5\text{H}_5\text{N}$ and $\text{CMeBr}(\text{CO}_2\text{Et})_2$ do not appear to react in C_6H_6 at 36° . Dicarbethoxymethylisoquinolinium enol-betaine, m.p. 195° , yields a perchlorate, m.p. $91\text{--}92^\circ$. The production of a betaine requires the presence of two strongly negative groups. Thus carbethoxymethylpyridinium bromide, m.p. $135\text{--}136^\circ$, does not give a coloured base with K_2CO_3 and CHCl_3 . Phenylcarbethoxymethylpyridinium bromide, m.p. $159\text{--}160^\circ$ (decomp.), from $\text{C}_5\text{H}_5\text{N}$ and $\text{CHPhBr}\cdot\text{CO}_2\text{Et}$, becomes pale red when treated with K_2CO_3 and the colour passes into CHCl_3 so that possibly an equilibrium exists between a colourless carbinol base and a coloured form. Phenylcarbethoxymethylisoquinolinium bromide, m.p. $104\text{--}105^\circ$, gives a perchlorate, m.p. $159\text{--}160^\circ$, and a nitrate. H. W.

Hydrolysis of azlactones with alcoholic potassium hydroxide. E. T. STILLER (J.C.S., 1937, 473–476).—2-Phenyl-4-(o -carbomethoxybenzylidene)-oxazolone (Bain *et al.*, J.C.S., 1914, 105, 2397) with KOH-MeOH or KOH-EtOH gives BzOH and, respectively, Me (I), m.p. $134\text{--}135^\circ$ ($\text{K} + 3\cdot5\text{H}_2\text{O}$ derivative) or Et 1-keto-1:2-dihydroisoquinoline-3-orthoformate, m.p. $183\text{--}185^\circ$, converted by boiling 2N-KOH into isocarbostyryl-3-carboxylic acid [Me (II), m.p. $161\text{--}162^\circ$, and Et (III), m.p. $147\text{--}148^\circ$, esters; amide, m.p. 289°] and by dil. HCl into (II) and (III), respectively. (I) in MeOH with $\text{Et}_2\text{O}\cdot\text{CH}_2\text{N}_2$ affords Me 1-keto-2-methyl-1:2-dihydroisoquinoline-3-orthoformate, m.p. $87\text{--}88^\circ$, converted by warm dil. HCl into the corresponding -3-carboxylate, m.p. $132\text{--}133^\circ$. The formation of orthoformates seems to be dependent on the presence of CO_2Alk on the adjacent nuclear C since MeOH-KOH and 2-phenyl-4-benzylideneoxazolone (Bain *et al.*, *loc. cit.*) give α -benzamidoacinnamic acid, and 2-phenyl-4-indolylideneoxazolone similarly affords indole-3-(α -benzamido)acrylic acid. J. W. B.

Condensation reactions of quinolinealdehydes. C. E. KWARTLER and H. G. LINDWALL (J. Amer. Chem. Soc., 1937, 59, 524–526).—Oxidation (SeO_2 in xylene at 135°) of 4-methylquinoline gives quinoline-4-aldehyde, m.p. $51\text{--}53^\circ$ [hydrate (I), m.p. $84\text{--}84\cdot5^\circ$; oxime, m.p. $181\text{--}182^\circ$; p -nitrophenylhydrazone, m.p. $261\text{--}262^\circ$], and/or quinoline-4-carboxylic acid. 6-Methoxyquinoline-4-aldehyde, m.p. $96\text{--}98^\circ$ (oxime, m.p. $214\text{--}216^\circ$), is similarly prepared. (I), MeNO_2 , and EtOH-NHET₃ afford α -nitro- β -hydroxy- β -4-quinolylethane, m.p. $133\text{--}136^\circ$; the hydrate (II) of quinoline-2-aldehyde (oxime, m.p. $188\text{--}190^\circ$; 2:4-dinitrophenylhydrazone, m.p. $251\text{--}253^\circ$) similarly gives α -nitro- β -hydroxy- β -2-quinolylethane, m.p. $110\text{--}113^\circ$. (I), COPhMe , and cold aq. EtOH-NaOH yield 4-diphenacilmethylquinoline, m.p. $144\text{--}146^\circ$ (di-oxime, m.p. $204\text{--}205^\circ$), whilst (II) similarly affords Ph β -hydroxy- β -2-quinolylethyl ketone, m.p. $114\text{--}116^\circ$ (also formed using NHET₃ as the condensing agent). (II) and COMe₂ in aq. EtOH-NaOH give β -hydroxy- β -2-quinolylethyl Me ketone, m.p. $164\text{--}167^\circ$; in EtOH-NHET₃, di-(β -hydroxy- β -2-quinolylethyl) ketone, m.p. $208\text{--}210^\circ$, results. H. B.

Calcium salts of substituted quinolinecarboxylic acids.—See B., 1937, 290.

Quinoline derivatives.—See B., 1937, 289.

(A) Condensation of acetylene with esters of aminobenzoic acids. (B) Condensation of acetylene with p -nitroaniline. New synthesis of 6-nitroquinaldine. N. KOZLOV and P. FEDOSEEV (J. Gen. Chem. Russ., 1937, 7, 51–53, 54–55).—(A) $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ in EtOH and C_2H_2 , in presence of HgCl_2 , yield cis- (I), m.p. $168\text{--}169^\circ$ and trans- γ -4-carbethoxyanilino- α -4-carbethoxyanilobutane, m.p. 184° . (I) decomposes when heated yielding Et quinaldine-6-carboxylate (picrate, m.p. 196°). $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ similarly yields γ -2-carbomethoxyanilino- α -2-carbomethoxyanilobutane, which gives on hydrolysis the corresponding 2:2'-dicarboxylic acid, decomp. $110\text{--}150^\circ$ to yield quinaldine.

(B) $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ in EtOH and C_2H_2 in pres-

ence of HgCl_2 yield *cis*-, m.p. 195° , and *trans*- α -*di-p-nitroanilino*- Δ^2 -*butene*, m.p. 231° , both converted by heating above the m.p. into 6-nitroquinaldine.

R. T.

Manufacture of quinaldine compounds.—See B., 1937, 290.

Catalytic hydrogenation of 2-cyano-1-benzoyl-1:2-dihydroquinoline (Reissert's compound). I. H. RUPE, R. PALTZER, and K. ENGEL [with, in part, GASSMANN and H. VON BIDDER] (Helv. Chim. Acta, 1937, 20, 209—218).—2-Cyano-1-benzoyl-1:2-dihydroquinoline (I) (Reissert, A., 1905, i, 247) is hydrogenated (Ni) at 80 — $90^\circ/100$ atm. in EtOAc to 2-benzamidomethyl-1:2:3:4-tetrahydroquinoline (II), m.p. 138 — 139° (*NO*-derivative, m.p. 156°), hydrolysed by HCl -EtOH- H_2O to 2-aminomethyl-1:2:3:4-tetrahydroquinoline (III), b.p. $168^\circ/11$ mm. (perchlorate, explodes when melted; picrate, m.p. 183° ; *H* oxalate, m.p. 159° ; tartrate, m.p. 152° ; citrate, m.p. 184°). (II) is converted by BzCl in anhyd. $\text{C}_6\text{H}_5\text{N}$ into 1-benzoyl-2-benzamidomethyl-1:2:3:4-tetrahydroquinoline, m.p. 164° , also obtained similarly from (III). (III) yields a phenylthiocarbamide, $\text{C}_{17}\text{H}_{19}\text{N}_3\text{S}$, m.p. 130° , and a *CHPh* derivative, m.p. 70 — 71° after softening at about 65° . (II) is transformed by MeI in MeOH at 100° into 1-methyl-2-benzamidomethyl-1:2:3:4-tetrahydroquinoline methiodide, m.p. 166° , converted by HCl into MeI and 1-methyl-2-aminomethyl-1:2:3:4-tetrahydroquinoline (IV), b.p. 153 — $155^\circ/11$ mm. (hydrochloride; perchlorate; picrate, m.p. 171° ; citrate, m.p. 164°), also obtained from 1-methyl-2-benzamidomethyl-1:2:3:4-tetrahydroquinoline. Treatment of (III) with NaOH and Me_2SO_4 gives ill-defined results whereas MeI and KOH in MeOH give 1-methyl-2-dimethylaminomethyl-1:2:3:4-tetrahydroquinoline methiodide (V), 1-methyl-2-dimethylaminomethyl-1:2:3:4-tetrahydroquinoline (VI), b.p. $144^\circ/11$ mm. (picrate, m.p. 122°), and (IV). Hydrolysis of (VI) with HCl gives (IV). (IV) is converted by MeI and KOH at 100° into (V) and (VI). Hydrogenation (Pd-black) at 80 — $90^\circ/115$ atm. of (I) gives (II) and (?) the compound, $(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NBz})_2$, m.p. 210° . H. W.

Synthesis of dihydrocarbostyryl and homodihydrocarbostyryl by ring enlargement and a synthesis of tetrahydroquinoline. L. H. BRIGGS and G. C. DE ATH (J.C.S., 1937, 456—457).—The action of N_3H -conc. H_2SO_4 on cyclic ketones (Schmidt, A., 1924, i, 721) has been extended to the aromatic series. Thus COPhMe gives NHPhAc ; α -hydriindone—5% N_3H -conc. H_2SO_4 in C_6H_6 at 40° give dihydrocarbostyryl (68% yield), and 1-keto-1:2:3:4-tetrahydronaphthalene (in CHCl_3) similarly gives homodihydrocarbostyryl (70% yield), hydrolysed (91% yield) by hot conc. HCl into γ -*o*-aminophenylbutyric acid. This with N_3H gives a 44% yield of γ -*o*-aminophenylpropylamine, the dihydrochloride of which affords a 50% yield of tetrahydroquinoline when distilled.

J. W. B.

Rupture of cyclic azomethines. Opening of the ring of 6:7-dimethoxyisoquinoline. M. I. KARAT SCHNIK and A. I. ZITZER (J. Gen. Chem. Russ., 1937 7, 162—168).—6:7-Dimethoxyisoquinoline (I) an

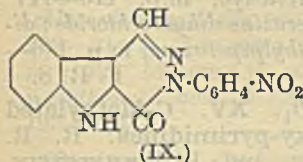
1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ in Et_2O yield 6:7-dimethoxy-N-2':4'-dinitrophenylisoquinoline chloride (II), m.p. 154 — 155° , converted by aq. NH_3 into 1-hydroxy-6:7-dimethoxy-2-(2':4'-dinitrophenyl)-1:2-dihydroisoquinoline, m.p. 162 — 163° (1-*O-Me*, m.p. 116 — 118° ; 1-*O-Et* derivative, m.p. 145 — 148°). The appropriate bases with (II) yield (I) and 2:4-dinitro- or 2:4-dinitro-4'-methyl-diphenylamine, or N-2':4'-dinitrophenylpiperidine.

R. T.

Reactions of 2:4-dimethylacetophenone with compounds of the thiocarbanilide type. K. DZIEWONSKI and J. MOSZEW (Bull. Acad. Polonaise, 1936, A, 258—265; cf. A., 1933, 836).—2:4- $\text{C}_6\text{H}_3\text{Me}_2\text{COMe}$ (I) with $\text{CS}(\text{NHPh})_2$ at 220° affords 4-anilino-2-m-xylylquinoline, m.p. 221° [hydrochloride, m.p. 184 — 185° (decomp.); picrate, m.p. 235 — 236° ; methiodide, m.p. 246 — 248° (decomp.); *NO*-, m.p. 141 — 142° (decomp.), N-*Ac*, m.p. 143 — 144° , and N-*Me*, m.p. 149° , derivatives], which with boiling EtOH-KOH under pressure gives 4-hydroxy-2-m-xylylquinoline, m.p. 255° . (I) with *s*-di-*p*-tolylthiocarbamide at 180 — 220° affords 4-*p*-toluidino-2-m-xylyl-6-methylquinoline, m.p. 191° [hydrochloride, m.p. 289° ; picrate, m.p. 245° ; methiodide, m.p. 233 — 234° ; N-*Me*, m.p. 157 — 158° , and -*Ac* derivative, m.p. 163°], which with EtOH-KOH at 200° gives 4-hydroxy-2-m-xylylquinoline, m.p. 237° . (I) with *s*-di-*m*-xylylthiocarbamide at 180 — 220° affords 4-m-xylylidino-2-m-xylyl-6:8-dimethylquinoline, m.p. 192° (picrate, m.p. 187 — 188° ; N-*Ac* derivative, m.p. 164°), converted by EtOH-KOH at 220° into 4-hydroxy-2-m-xylyl-6:8-dimethylquinoline, m.p. 234 — 235° . J. L. D.

Synthesis of norharmancarboxylic acid and its bearing on the constitution of lysergic acid. H. KING and E. T. STILLER (J.C.S., 1937, 466—473).—*Me* indole-2-carboxylate with $\text{Zn}(\text{CN})_2\text{-HCl}$ in Et_2O and subsequent hydrolysis gives 2-carbomethoxyindole-3-aldehyde, m.p. 209 — 210° , isolated as its *anil*, m.p. 163 — 164° . 2-Carbomethoxy- and 2-carbomethoxy-indole-3-aldehyde with $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}\cdot\text{NaOAc}\cdot\text{Ac}_2\text{O}$ afford, respectively, 2-phenyl-4-(2'-carbomethoxyindolylidene)oxazolone (I), m.p. 253 — 254° , and the corresponding carbomethoxy-azlactone (II), m.p. 249 — 250° [lit., m.p. 242° (decomp.)]. Hydrolysis of (II) with 8% aq. KOH gives 2-carboxyindole-3-(α -benz-amido)-acrylic acid, + EtOH (III), m.p. 223 — 224° , and + AcOH , m.p. 233 — 234° [*Et*_, m.p. 198 — 199° , and *Me*_, m.p. 230 — 231° (decomp.)], esters, by hydrolysis of (II) with ROH-anhyd. Na_2CO_3 . (II) with EtOH-aq. NH_3 gives 2-carbomethoxyindole-3-(α -benz-amido)acrylamide, m.p. 246 — 247° , resolidifying at 249° , converted by hot 2*N*- NaOH into the *Na* salt + $3\text{H}_2\text{O}$ of 5-keto-2-phenyl-4-(2'-carboxyindolylidene)-4:5-dihydroglyoxaline, which is obtained by acidification. Hydrolysis of (I) or (II) with boiling MeOH-KOH or with NaOMe-MeOH affords 2-keto-2:3-dihydro- β -carboline-4-carboxylic acid (IV), m.p. 365° (decomp.) (separates at its *K* salt; *Me*_, m.p. 272 — 273° , and *Et*_, m.p. 260 — 261° , esters), *Me* 2-keto-2:3-dihydro- β -carboline-4-orthoformate (V), dimorphous, + EtOH, m.p. 233 — 234° (decomp.) and m.p. 232 — 233° [*K*_, + $6\text{H}_2\text{O}$ (VI), and *Na*_, + $6\text{H}_2\text{O}$, derivatives], (III), *BzOH*, and, probably, 2-carboxy-

indole-3-pyruvic acid. (V) with CH_2N_2 or (VI) with MeI gives *Me* 2-keto-3-methyl-2:3-dihydro- β -carboline-4-orthoformate, m.p. 262–263° (decomp.) (? m.p. 283–284°), converted by warm dil. HCl into the 4-carboxylate, m.p. 256–258°, but (V) with $\text{Me}_2\text{SO}_4 \cdot \text{K}_2\text{CO}_3$ in dry COMe_2 affords *Me* 2-keto-1:3-dimethyl-2:3-dihydro- β -carboline-4-carboxylate, m.p. 160–161°. Similar products are obtained from (II) and $\text{EtOH} \cdot \text{KOH}$, *Et* 2-keto-2:3-dihydro- β -carboline-4-orthoformate + 0.5EtOH having m.p. 192–193°. (IV) with $\text{PCl}_5 \cdot \text{POCl}_3$ and treatment of the product with MeOH gives *Me* 2-chloro- β -carboline-4-carboxylate (VII), m.p. 244–245° [hydrochloride, m.p. 231–232° (decomp.)]; hydrolysed by hot 2*N*-NaOH to the free acid + H_2O , m.p. 246–247° (decomp.), and the dihydrochloride, m.p. 213–214° (decomp.), of a base, $\text{C}_{25}\text{H}_{20}\text{O}_4\text{N}_4$, m.p. 333–334° (decomp.). (VII) with HI (*d* 1.7)–red P–KI at 180° gives norharmanicarboxylic acid + 1.5AcOH (VIII), m.p. 309–310° (decomp.) [*Me* ester, m.p. 262° (decomp.)], decarboxylated by heating with $\text{Ca}(\text{OH})_2$ to norharman, and converted by $\text{MeOH} \cdot \text{Et}_2\text{O} \cdot \text{CH}_2\text{N}_2$ into *Me* 1-methyl- β -carboline-4-carboxylate, m.p. 256–257°. The *p*-nitrophenylhydrazine,



m.p. 274–275° (decomp.), of 2-carbethoxy- and of 2-carbomethoxy-indole-3-aldehyde, crimson converted into colourless needles without melting at 287–292°, are converted at 290–300°/reduced pressure into 2-*p*'-nitrophenylindolo-(2':3':4:5)-pyridaz-3-one (IX), m.p. >365°. (VIII) does not give the usual indole reactions and lysergic acid probably does not contain a β -carboline skeleton.

J. W. B.

Reaction between anthranilic acid and cyclopentanone. B. K. BLOUNT and S. G. P. PLANT (J.C.S., 1937, 376–377).—Anthranilic acid (I) and cyclopentanone at 265° afford 12-keto-3-cyclopentylidene-2:3:5:12-tetrahydro- β -quinindene, (II), m.p. 285°, also formed from (I) and cyclopentylidenecyclopentanone. With POCl_3 , (II) affords 12-chloro-3-cyclopentylidene-2:3-dihydro- β -quinindene, m.p. 110°, whilst 12-keto-2:3:5:12-tetrahydro- β -quinindene gives 12-chloro-2:3-dihydro- β -quinindene, m.p. 70°.

J. D. R.

Meso-derivatives of acridine. VII. Preparation of 5-*p*-dimethylaminophenylacridines. N. S. DROZDOV (J. Gen. Chem. Russ., 1937, 7, 219–226).—5-Chloroacridine and NPhMe_2 in presence of AlCl_3 (3 hr. at 100°) yield 5-*p*-dimethylaminophenylacridine (I), m.p. 290°. The 3-Me derivative of (I) is prepared analogously. 1:3-Dinitroacridone, NPhMe_2 , and POCl_3 (100°; 3 hr.) yield 1:3-dinitro-5-*p*-dimethylaminophenylacridine, m.p. 268–270° (decomp.). 4-Nitro-4'-methylidiphenylamine-2-carboxylic acid and POCl_3 in xylene (130–170°) yield 5-chloro-7-nitro-3-methylacridine, m.p. 199–200°, converted by heating with PhOH into 7-nitro-5-phenoxy-3-methylacridine, m.p. 189–190°, and with aq. NaOH into 7-nitro-3-methylacridone, m.p. >300°, which with NPhMe_2 and POCl_3 gives 7-nitro-5-*p*-dimethylaminophenyl-3-methylacridine, m.p. 259–260°.

R. T.

2:8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-group on the 5-carbon atom. XV. Synthesis of 2:8-diethoxy-5-alkylamino-10-ethylacridinium derivatives. K. ISHIIHARA (J. Chem. Soc. Japan, 1935, 56, 1164–1173).—The following 5-alkyl derivatives are described: *Iodides*: *Me*, m.p. 227°; *Et*, m.p. 224°; *Pr*^a, m.p. 207°; *Bu* ^{β} , m.p. 230°; iso- C_5H_{11} , m.p. 227°. *Hydroxides*: *Me*, m.p. 126°; *Et*, m.p. 115°; *Pr*^a, m.p. 105°; *Bu* ^{β} , m.p. 122°; iso- C_5H_{11} , m.p. 101°. *Chlorides*: *Me*, m.p. 225°; *Et*, m.p. 216°; *Pr*^a, m.p. 230°; *Bu* ^{β} , m.p. 194°; iso- C_5H_{11} , m.p. 152°. *Oxalates*: *Me*, m.p. 195°; *Et*, m.p. 180°; *Pr*^a, m.p. 174°; *Bu* ^{β} , m.p. 199°; iso- C_5H_{11} , m.p. 172°.

CH. ABS. (r)

Differences in absorption curves of groups of unsaturated hydantoin. M. K. SEIKEL (J. Amer. Chem. Soc., 1937, 59, 436–439).—The characteristic ultra-violet absorption spectrum of anisylidene-hydantoin is not appreciably affected by 3(*N*)-substitution; such compounds may exist largely in the enolic forms. Distinct changes occur with 1(*N*)-substitution irrespective of the presence or absence of a 3-substituent. The stable and labile geometrical isomerides of the 1:3-disubstituted derivatives also show differences. The uniformity of absorption of each group parallels chemical and other physical properties.

H. B.

Synthesis of 4-(or 5)-carbamidoglyoxaline. G. HUNTER and I. HLYNKA (Biochem. J., 1937, 31, 488–489).—4-(or 5)-Nitroglyoxaline was reduced with Na–Hg and the aminoglyoxaline treated, without isolation, with HCNO . The product had the same m.p. and mixed m.p. as that obtained from guanine (A., 1936, 999, 1000).

P. W. C.

Iminazoles. IV. Derivatives of glyoxaline. R. WEIDENHAGEN, R. HERRMANN, and H. WEGNER (Ber., 1937, 70, [B], 570–583; cf. A., 1936, 1523).—The synthesis (*loc. cit.*) is extended to ketols with *sec.* OH. Thus, furoin, CH_2O , $\text{Cu}(\text{OAc})_2$, and conc. NH_3 in MeOH yield 4:5-difurylglyoxaline, m.p. 162–163° (decomp.) [*Cu* salt; hydrochloride, m.p. 196° (decomp.)]; picrate, m.p. 222–223° (decomp.) after darkening]. Analogously, furfuraldehyde (I) yields 2:4:5-trifurylglyoxaline, m.p. 202° (darkening) [hydrochloride, m.p. 141°]. Acetoin gives 4:5-dimethylglyoxaline (hydrochloride, m.p. 285°) and 2:4:5-trimethylglyoxaline (hydrochloride, m.p. 310–311°; picrate, m.p. 157°). Benzoin affords 4:5-diphenylglyoxaline [picrate, m.p. 231–232° (lit. m.p. 135°)] and 2:4:5-triphenylglyoxaline (picrate, m.p. 235°). Fructose and CH_2O afford 4(5)-hydroxymethylglyoxaline in almost 40% yield owing to preliminary fission into $\text{CO}(\text{CH}_2\text{OH})_2$ and $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHO}$, which is further oxidised; glucose and invert sugar act similarly. *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OAc}$ and CH_2O yield 4(5)-*p*-tolylglyoxaline, m.p. 116–117° (picrate, m.p. 210°). 4(5)-*p*-Ethylphenylglyoxaline, m.p. 127–128° (picrate, m.p. 197°), is described. *p*-isoPropylbenzoylcarbinyl acetate, m.p. 40–41°, is hydrolysed to the corresponding carbinol, which affords 4(5)-*p*-isopropylphenylglyoxaline, m.p. 114–115° (picrate, m.p. 186–187°). The halogens in 4(5)-*p*-chlorophenyl-, m.p. 147° (picrate, m.p. 219–220°), and -*p*-bromo-

phenyl-, m.p. 142° (*picrate*, m.p. 216°), *-glyoxaline* do not react with Mg in Et₂O or isoamyl ether or with Na₂AsO₃ under pressure. 2-C₁₀H₇·CO·CH₂·OH gives 4(5)-2'-*naphthylglyoxaline* (II), m.p. 170—171° [*hydrochloride*, m.p. 219—220° after softening; *nitrate*, m.p. 185° (decomp.); *picrate*, m.p. 215°]. CH₂Bz·OH and (I) afford 2-furyl-4(5)-*phenylglyoxaline*, m.p. 180° (decomp.) [*hydrochloride*, m.p. 275—276°; *picrate*, m.p. 204° (decomp.)]. 4(5)-*p*-Carboxyphenylglyoxaline in NaOH is converted by gradual addition of the requisite amount of I into *iodo*-, m.p. 240° (decomp.), and *di-iodo*-, m.p. 234—235° (decomp.), 4(5)-*p*-carboxyphenylglyoxaline. Glyoxaline-4(5)-*p*-phenylsulphonic acid is iodinated to 2:5(4)-*di-iodoglyoxaline*-4(5)-*p*-phenylsulphonic acid, decomp. 327°; an I-derivative could not be obtained. Entry of I into glyoxaline-4(5)-carboxylic acid is accompanied by loss of CO₂ and gives 2:4:5-triiodoglyoxaline. (II) and fuming H₂SO₄ (10% SO₃) at 100° yield 4(5)-2'-*naphthylglyoxalinesulphonic acid*. 4(5)-Phenylglyoxaline is transformed by pyridinium-1-sulphonic acid into 4(5)-*phenylglyoxaline*-1-sulphonic acid, decomp. >300° after becoming transparent at 210° (*K* salt, anhyd. and +0.5H₂O). 4(5)-2'-*Naphthylglyoxaline*-1-sulphonic acid, becoming gelatinous at 200—210° (*K* salt), and *benzimidazole*-1-sulphonic acid, m.p. 221—222° (*K* salt), are obtained analogously. H. W.

Method for protecting the iminazole ring of histidine during certain reactions and its application to the preparation of *l*-amino-*N*-methylhistidine. V. DU VIGNEAUD and O. K. BEHRENS (J. Biol. Chem., 1937, 117, 27—36).—*l*-Histidine monohydrochloride when treated in dry liquid NH₃ with Na then with CH₂PhCl yields 1(or 3)-*benzyl-l-histidine* (I), m.p. 248—249°, [α]_D²⁵ +20.5° in H₂O + 1 equiv. of HCl, and some *amino-N-benzyl*-1(or 3)-*benzyl-l-histidine*, m.p. 193—195°, [α]_D²⁵ +34.5° in H₂O + 1 equiv. of HCl. *p*-C₆H₄Me·SO₂Cl·NaOH with (I) gives *N-p-toluenesulphonyl*-1(or 3)-*benzyl-l-histidine* (II), m.p. 198°, which on methylation (MeI·NaOH·H₂O; 68—70°; 40 min.) gives *p-toluenesulphonyl*-1(or 3)-*benzyl-N-methyl-l-histidine* (III), m.p. 118—122°. Na in liquid NH₃ reduces (I) and (II) to histidine without racemisation. Similarly, (III) is reduced in good yield to *l*-amino-*N-methylhistidine*, m.p. 266°, [α]_D²⁵ -13.5° in H₂O (mono-, m.p. 268°, and *di*-, m.p. 124—127°, *-hydrochloride*; *dipicrate*, m.p. 61°). All m.p. are corr. Other applications of the protection of the glyoxaline ring by benzylation followed by debenylation are suggested. H. G. M.

l-Histidine anhydride dihydrochloride, decomp. 270—280°, [α]_D²⁵ +48.1°.—See A., III, 141.

Rearrangement of pyrazolones and of their derivatives. I. A. KOCWA (Bull. Acad. Polonaise, 1936, A, 266—275).—Equimol. amounts of 1-phenyl-5-methylpyrazol-3-one (I) with CO(NHPh)₂ or PhNCO at 250—260° afford 4-carbanilido-1-phenyl-5-methylpyrazolone (II), m.p. 258°. Similarly, (I) with CS(NHPh)₂ or PhNCS affords 4-thiocarbanilido-1-phenyl-5-methylpyrazolone, m.p. 238°, which with NH₃ under pressure at 150—160°, or with PCl₅ at 130°, affords (II). α -C₁₀H₇·NCO and (I) similarly afford 4-carb- α -naphthylamido-1-phenyl-5-methyl-

pyrazolone, m.p. 231—232°. 1-Phenyl-2:3-dimethylpyrazolone (III) with CO(NHPh)₂ and ZnCl₂ at 260° affords 4-carbanilido-1-phenyl-2:3-dimethylpyrazolone (IV), m.p. 250°, also prepared from (III), PhNCO, and AlCl₃. With an equimol. amount of CS(NHPh)₂ or PhNCS at 230° (III) affords 4-thiocarbanilido-1-phenyl-2:3-dimethylpyrazolone (V), m.p. 199°, which when hydrolysed (NH₃, EtOH-HCl) or oxidised (warm Cr₂O₃, H₂O₂ or HNO₃) affords (IV) and with HNO₃ (*d* 1.48) gives a NO₂-compound, m.p. 240°. Et 1-phenyl-2:3-dimethylpyrazolone-4-carbithionate when boiled with NH₂Ph affords 1-phenyl-2:3-dimethyl-4-anilothiolmethylpyrazolone, R·C(NPh)·SH, m.p. 148°, isomeric with (V) and converted by hot EtOH-KOH into (IV). J. L. D.

Thiobarbituric acid compounds.—See B., 1937, 290.

Stereoisomeric 2:3:5:6-tetramethylpiperazines. V. F. B. KIPPING (J.C.S., 1937, 368—369). Separation of commercial 2:3:5:6-tetramethylpiperazine gives 99—99.5% of the α - and β -isomerides, with some δ - and ϵ -compounds, the last-named isolated as the (NO)₂-derivative, m.p. 116—117° (ϵ -2:3:5:6-tetramethylpiperazine dihydrochloride; *di-benzoyl*- ϵ -2:3:5:6-tetramethylpiperazine, m.p. 146—147°). F. R. S.

Crystalline vitamin-B₁. XV. C-Methylated 6-amino- and 6-hydroxy-pyrimidines. R. R. WILLIAMS, A. E. RUEHLE, and J. FINKELSTEIN. XVI. Identification of pyrimidine portion. J. K. CLINE, R. R. WILLIAMS, A. E. RUEHLE, and R. E. WATERMAN (J. Amer. Chem. Soc., 1937, 59, 526—530, 530—533).—XV. Oxidation (H₂O₂ at >90°) of 4-methyl-2-thiouracil, thiothymine, and 6-hydroxy-4:5-dimethyl-2-thiopyrimidine, m.p. >255° [from CHMeAc·CO₂Et and CS(NH₂)₂ in EtOH-NH₃], gives 6-hydroxy-4-methyl-, m.p. 148—149°, -5-methyl-, m.p. 153—154°, and -4:5-dimethyl-, m.p. 202—203°, -pyrimidine, respectively. 6-Amino-4-methyl-, m.p. 194—195°, -5-methyl-, m.p. 175—176°, and -4:5-dimethyl-, m.p. 229—231°, -pyrimidines are prepared from the respective 6-Cl-derivatives and EtOH-NH₃ at 110—120°. 6-Hydroxy-2:5-dimethylpyrimidine, m.p. 174° (from Et sodioformylpropionate and acetamide hydrochloride in H₂O), is similarly converted through the 6-Cl-derivative into 6-amino-2:5-dimethylpyrimidine, m.p. 201—202° (*picrate*, m.p. 222°). Ultra-violet absorption spectra of 6-hydroxy- and 6-aminopyrimidines and their 2-, 4-, and 5-Me, and 2:4-, 2:5-, and 4:5-Me₂ derivatives are given; the effect of acid and alkali on the NH₂-derivatives is discussed.

XVI. A more detailed account of work previously reviewed (A., 1936, 1159). The base, C₆H₁₀N₄, m.p. 211—215° (*picrate*, m.p. 225°) (cf. Windaus *et al.*, *ibid.*, 253), obtained by cleavage of vitamin-B₁ (I) with liquid NH₃, probably contains 6-NH₂ and a side-chain NH₂. 6-Hydroxy-2-methyl-5-ethoxymethylpyrimidine and aq. NaHSO₃ at 144°/sealed tube give the 5-sulphomethyl derivative, m.p. >360°, which is identical with the hydroxysulphonic acid previously prepared (A., 1935, 1035) from (I). 4:6-Diamino-5-ethylpyrimidine, m.p. 245° (lit. 233—235°) (*dipicrate*, m.p. 165—167°), is obtained from

4-iodo-6-amino-5-ethylpyrimidine and EtOH-NH_3 at 220° . 6-Amino-2:5-dimethylpyrimidine is formed from the aminosulphonic acid (*loc. cit.*) [from (I)] and Na in liquid NH_3 . H. B.

Aryloxy-derivatives of pyrimidines, quinoxalines, and quinolines. (MISS) D. LOCKHART and E. E. TURNER (J.C.S., 1937, 424–427).—Condensation of 2:4:6-trichloropyrimidine or 2:3-dichloroquinoxaline with the appropriate phenoxide or amine gives 2:4:6-*tri-phenoxy*-, m.p. 156° , -*p-tolyloxy*-, m.p. 118° , -*p-anisoxo*-, m.p. 120° , and -*p-chlorophenoxy-pyrimidine*, m.p. 107° ; 2:3-*di-phenoxy*-, m.p. 160° , -*p-tolyloxy*-, m.p. 145 – 146° , -*p-anisoxo*-, m.p. 193 – 194° , -*p-chlorophenoxy*-, m.p. 153° , -*anilino*-, m.p. 223° , -*m-toluidino*-, m.p. 225° , and -*p-toluidino-quinoxaline*, m.p. 254° . 4-*Chloro-6-ethoxy-2-methylquinoline*, m.p. 65° , from the OH-compound, is nitrated to the 4-*chloro-5-nitro*-derivative, m.p. 125° , which with the required phenoxide gives 5-*nitro-4-p-anisoxo-6-ethoxy*-, m.p. 109° , 4-*phenoxy-2-ethoxy*-, m.p. 107 – 108° (methiodide, m.p. 210°); 4-*p-anisoxo*-, m.p. 115° (methiodide, m.p. 216°), -*tolylloxy*-, m.p. 134° (methiodide, m.p. 213°), and -*chlorophenoxy-6-ethoxy*-, m.p. 125° (methiodide, m.p. 213 – 214°); 4-*m-nitro*-, m.p. 183 – 184° [methiodide, m.p. 224° (decomp.)], -*amino*-, m.p. 139° , and -*bromo-p-methoxyphenoxy-6-ethoxy-2-methylquinoline*, m.p. 193 – 194° . F. R. S.

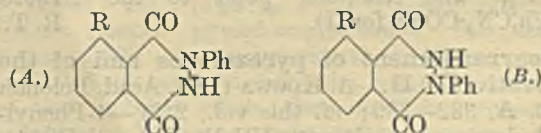
Pyrimidine derivatives. A. BOWMAN (J.C.S., 1937, 494–495).—The following are prepared by adaptation of known methods: 2:4:6-*trimethylpyrimidine*, b.p. 160° , and its *dihydrate*, m.p. 47 – 48° (compound, m.p. 169° , with HgCl_2), converted by PhCHO-ZnCl_2 at 150° into 2:4:6-*tristyrilpyrimidine*, m.p. 198 – 199° ; 2-*phenylpyrimidine-4:6-dicarboxylic acid*, decomp. 165° , m.p. dependent on the rate of heating; 2-*phenyl-4-methylpyrimidine-6-carboxylic acid*, m.p. 112° (decomp.); 2:4-*dichloro-5-chloro-methyl-6-methylpyrimidine*, m.p. 38 – 39° ; and 3-(2':4'-*dichloro-6'-methylpyrimidyl-5'-methyl*)-5- β -*hydroxyethyl-4-methylthiazolium chloride*, sinters 201° , m.p. 202.5° , which does not exhibit aneurin-like activity. J. W. B.

Synthesis of 1-d-ribosidouracil. Interaction of acetobromo-d-ribose and 2:4-diethoxypyrimidine. G. E. HILBERT and C. E. RIST (J. Biol. Chem., 1937, 117, 371–380).—Acetobromo-d-ribose with 2:4-diethoxypyrimidine (65° ; 18 hr.) yields some uracil, 4-*ethoxy-2-triacetyl-d-ribosidopyrimidine* (I), m.p. 162.5° , $[\alpha]_D^{25}$ -66.2° in CHCl_3 , and a syrupy product, which on hydrolysis yields some 1-d-*ribosidouracil*, m.p. 257 – 258° , $[\alpha]_D^{25}$ -140.0° in H_2O [Ac_3 derivative, m.p. 184 – 185° (when heated slowly), $[\alpha]_D^{25}$ -25.1° in CHCl_3]. This is similar in chemical but not in physical properties to uridine (1-d-*ribosidouracil-furanose* form), and probably is a pyranoside. (I) is hydrolysed by 5% HCl giving uracil, and by $\text{NaOH-H}_2\text{O-COMe}_2$ giving 2-*keto-4-ethoxy-1:2-dihydropyrimidine*. H. G. M.

Chemiluminescence of cyclic hydrazides. R. WEGLER (J. pr. Chem., 1937, [ii], 148, 135–160).—The chemiluminescence of hydrazides in presence of H_2O_2 is greatly enhanced by the use of radish or

horseradish shavings or expressed juice; it does not quite attain the intensity given by haemin (I) but persists for several days since decomp. of H_2O_2 is nearly avoided if the materials are pure. (I) causes much more intense luminescence in strongly than in feebly alkaline solution whereas closely related derivatives are inactive. In spite of marked catalytic activity, various Fe oxides do not enhance luminescence. The importance of the oxidisability of *m-NH}_2* in 3-aminophthalhydrazide (II) is established by the observation that 3-*hydrazinophthalhydrazide* (III), m.p. (indef.) 280 – 300° (decomp.), is more strongly luminescent than (II) whilst the diazonium salt from (II) is intensely luminescent; in each case addition of (I) has little effect. Under all conditions the activity of the :CHPh derivative, m.p. 310 – 312° , of (III) is less marked than that of (III) or (II). In spite of ready oxidisability 3:5-diaminophthalhydrazide (obtained impure from 3:5-dinitrophthalhydrazide, m.p. 306 – 307°) is less luminescent than (II); *diaminopyromellitidihydrazide*, m.p. 42° and m.p. $>250^\circ$ after re-solidification at 68 – 69° (obtained from *dinitropyromellithydrazide*, m.p. $>260^\circ$), is scarcely luminescent. The luminescence of 3-*hydroxyphthalhydrazide*, m.p. about 300° (much decomp.), is intermediate between that of (II) and phthalhydrazide (IV) and $>$ that of 3:6-*dihydroxyphthalhydrazide*, m.p. $>340^\circ$, although the latter is readily oxidised and rapidly becomes coloured when its alkaline solutions are exposed to air. Hydrazides of polycyclic ring systems (e.g., anthraquinone-2:3-dicarboxyhydrazide) are less luminescent than (IV). The behaviour of succinhydrazide proves that the saturated character of the azine ring is not an impediment and that the presence of a second ring is not essential for luminescence. Dimethylmaleinhydrazide shows the expected action also exhibited by dimethylmalonhydrazide with a 5-membered ring. *Pyridine-2:3-dicarboxyhydrazide*, m.p. 309° , is about as strongly luminescent as (IV). In study of the effect of substitution in the azine ring (IV) is transformed by the action of CH_2PhCl on the Ag salt into the O-*benzyl* derivative,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{O-CH}_2\text{Ph})\text{N} \end{smallmatrix} \text{NH}$, m.p. 156° , which is highly luminescent; the isomeric N-*benzyl* compound, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO-NH} \\ \diagup \quad \diagdown \\ \text{CO-N-CH}_2\text{Ph} \end{smallmatrix}$, m.p. 204° [from $\text{CH}_2\text{Ph-NH-NH}_2$ and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$], is distinctly but feebly active. The ease with which CH_2Ph is eliminated renders these compounds of somewhat doubtful val. Direct treatment of $\text{NO}_2\text{-C}_6\text{H}_3(\text{CO}_2\text{H})_2$ with NHPh-NH_2 at 210° gives products sol. in alkali and converted by reduction (Zn-AcOH-HCl) into compounds almost insol. in alkali and hence probably consisting of a mixture of the forms A and B ($\text{R} = \text{NO}_2$ or NH_2). The behaviour of these products appears to show

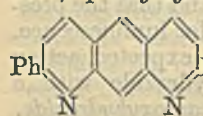


that chemiluminescence is possible in hydrazides substituted at N. The following compounds are incidentally described: 2:3-*quinoxalinecarboxyhydraz-*

ide, m.p. $>330^\circ$; *phthal*-NN'-dibenzylhydrazide, m.p. 153—154°; *phthal*-ON-dibenzylhydrazide, m.p. 96—97°; 3-nitrophthalpropylhydrazide, m.p. 207—210°; 3-nitrophthalpropylhydrazide, m.p. 119°, and the 3-NH₂-compound, m.p. 142°. H. W.

Heterocyclic compounds containing nitrogen.

XXVIII. 4:6-Dinitro- and -diamino-isophthalaldehyde. P. RUGGLI and P. HINDERMAN (Helv. Chim. Acta, 1937, 20, 272—282).—4:6-Dinitro-*m*-xylene is condensed with *p*-NO₂-C₆H₄-NMe₂ and Na₂CO₃ in EtOH and the product is oxidised by HNO₃ (*d* 1.12) in C₆H₆ to 4:6-dinitroisophthalaldehyde (I), m.p. 129.5—130°. (I) is decomposed by NaOH or Na₃PO₄ and converted by C₅H₅N into a substance, decomp. $>360^\circ$. (I) yields a (NaHSO₃)₂ compound, a dianil, m.p. 164.5—165°, and a disemicarbazone, decomp. $>360^\circ$. Condensation of (I) with CH₂(CO₂H)₂ in C₅H₅N at 50—55° gives 4:6-dinitrophenylene-1:3-diacrylic acid, m.p. 216°; the Et₂ ester, m.p. 116°, is reduced (Ni-EtOAc-EtOH-H₂O) to Et₂ 4:6-diaminophenylene-1:3-diacrylate, m.p. 195—196° (hydrochloride; Ac₂ derivative, m.p. 244—245°). 4:6-Dinitroisophthalaldibarbaturic acid is described. (I) and CH₃N₂ in Et₂O give 4:6-dinitro-1:3-diacetylbenzene, m.p. 153—154°. (I) is not reduced satisfactorily in presence of Ni but is readily transformed by FeSO₄ and NH₃ into 4:6-diaminoisophthalaldehyde (II), m.p. 208°, in 85% yield. (II) is stable towards NaOH; it gives a dioxime, m.p. 219—220° after becoming discoloured at 210°, a disemicarbazone, slow decomp. $>360^\circ$, a mono-, m.p. 275—276° (decomp.), and a di-, decomp. 337°, -phenylhydrazone. (II) is slowly converted by Ac₂O at room temp. into the Ac₂ derivative, m.p. (indef.), 270—272° (decomp.) after softening at 250°, transformed by boiling Ac₂O into 4:6-diacetamidisophthalaldehyde, decomp. 280—282° after softening at 270°. (II) condenses with C₆H₅Me in presence of KOH-MeOH to 2:8-diphenyl-lin.-dipyridinobenzene (III), m.p. 216—217° (dipicrate, incipient decomp. 270°), and with CH₃Ac-CO₂Et to Et₂ 2:8-dimethyldipyridinobenzene-3:7-dicarboxylate, m.p. 166—167° (dipicrate).



(III).

280—282° after softening at 270°. (II) condenses with C₆H₅Me in presence of KOH-MeOH to 2:8-diphenyl-lin.-dipyridinobenzene (III), m.p. 216—217° (dipicrate, incipient decomp. 270°), and with CH₃Ac-CO₂Et to Et₂ 2:8-dimethyldipyridinobenzene-3:7-dicarboxylate, m.p. 166—167° (dipicrate).

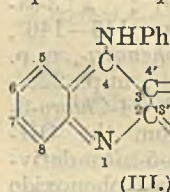
H. W.

Structure of the product of reaction of α -dibromo- β -phenylethyl methyl ketone with salts of azoimide. S. G. FRIDMAN (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 587—604).—The mono-azide (I), m.p. 78—79°, previously described (A., 1936, 1109) evolves N₂ and NH₃ when treated with aq. NaOH, yields PhCHO with NaOH or H₂SO₄, and BzOH with KMnO₄, and combines with Br or Cl₂ to yield unidentified halogen derivatives, with evolution of N₂. The reactions point to the structure CHPh.CN₂.COMe for (I).

R. T.

Rearrangement of pyrazolones and of their derivatives. II. A. KOCWA (Bull. Acad. Polonaise, 1936, A, 382—389; cf. this vol., 212).—1-Phenyl-5-methylpyrazolone (I) with NH₂Ph, HCl and POCl₃ at 260° affords 3-anilo-1-phenyl-5-methylpyrazolone (II), m.p. 146—147° [picrate, m.p. 194° (decomp.)], which with an equimol. amount of CO(NHPh)₂ or PhNCO

at 230—240° affords 4-anilino-1'-phenyl-5'-methylpyrazolo-3':4':2:3-quinoline (III), m.p. 198—199° [hydrochloride, m.p. 273—274° (decomp.)]; picrate, m.p. 209°. (III) with EtOH-KOH at 200—220° gives 4-hydroxy-1'-phenyl-5'-methylpyrazolo-3':4':2:3-quinoline, m.p. 189° (decomp.). Equimol. amounts of (II) and CS(NHPh)₂ or PhNCS at 230—240° afford (III) and 3-anilo-4-thiocarbanilido-1-phenyl-5-methylpyrazolone, m.p. 224—225°, which at 100—110° with PCl₅ gives (III). (I) with *p*-C₆H₄Me:NH₂, HCl and POCl₃ at 260—270° affords 3-*p*-toluido-1-phenyl-5-methylpyrazolone, m.p. 116°



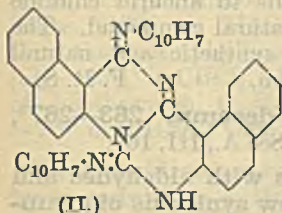
(III).

(picrate, m.p. 203°), which with an equimol. amount of PhNCS at 240—245° gives 4-anilino-1'-phenyl-5':6-di-methylpyrazolo-3':4':2:3-quinoline, m.p. 192—193°, converted by EtOH-KOH at 200—220° into 4-hydroxy-1'-phenyl-5':6-dimethylpyrazolo-3':4':2:3-quinoline, m.p. 203° (decomp.). J. L. D.

Rearrangement of pyrazolones and of their derivatives. III. A. KOCWA (Bull. Acad. Polonaise, 1936, A, 390—402; cf. preceding abstract).—An equimol. mixture of 5-anilo-1-phenyl-3-methylpyrazolone (I) with CO(NHPh)₂, CS(NHPh)₂, PhNCO, or PhNCS at 245—250° in 0.5 hr. affords 4-anilino-1'-phenyl-3'-methylpyrazolo-4':5':2:3-quinoline (II), m.p. 170° [hydrochloride, m.p. 265° (decomp.)]; picrate, m.p. 256—257° (decomp.); NO-derivative, m.p. 170° (decomp.)], converted by aq. EtOH-KOH at 200—220° into 4-hydroxy-1'-phenyl-3'-methylpyrazolo-4':5':2:3-quinoline, m.p. 274°, which when heated with NH₃ under pressure is converted into the 4-NH₂-compound, m.p. 150°. (I) with PhNCO at 260° for 10 min. affords 5-anilo-4-carbanilido-1-phenyl-3-methylpyrazolone, m.p. 171—172° [methiodide, m.p. 110—115° (decomp.)], with boiling 15% NaOH affords 5-anilo-4-carbanilido-1-phenyl-2:3-dimethylpyrazolone, m.p. 215—216°, which is not converted into a pyrazoquinoline derivative with P₂O₅, but with conc. HCl under pressure gives 5-anilo-1-phenyl-2:3-dimethylpyrazolone, converted by P₂O₅ into (II), and with HCl under pressure into (I). (I) with α -C₁₀H₇-NCO (III) at 290° affords 4- α -naphthylamino-1'-phenyl-3'-methylpyrazolo-4':5':2:3-quinoline, m.p. 198° [picrate, m.p. 224° (decomp.)]; NO-derivative, decomp. at 145°, and a substance, m.p. 314° (decomp.). 5-*p*-Toluido-1-phenyl-3-methylpyrazolone (IV) with CO(NHPh)₂, PhNCO, CS(NHPh)₂, or PhNCS at 235—240° affords 4-anilino-1'-phenyl-3':6-dimethylpyrazolo-4':5':2:3-quinoline, m.p. 174—175° [hydrochloride, m.p. 257° (decomp.)]; picrate, m.p. 234° (decomp.); NO-derivative, m.p. 174° (decomp.); 4-OH-analogue (V), m.p. 258°. (IV) with an equimol. amount of (III) at 280—285° affords 4- α -naphthylamino-1'-phenyl-3':6-dimethylpyrazolo-4':5':2:3-quinoline, m.p. 238—239° [picrate, m.p. 195°]; 4-OH-analogue identical with (V)]. J. L. D.

Reactions of β -naphthylamine with thiocarbamide. K. DZIEWOŃSKI, L. STERNBACH, and A. STRAUCHEN (Bull. Acad. Polonaise, 1936, A, 493—500).— β -C₁₀H₇-NH-CS-NH₂ or equimol. amounts of β -

$C_{10}H_7 \cdot NH_2$ and $CS(NH_2)_2$ at 230–240° under reduced pressures afford 2-thio-2:4-diketo-5:6-benzo-1:2:3:4-tetrahydroquinazoline-4- β -naphthyl (I), m.p. 318°; if the reaction temp. is raised to 300° 4:2'-diketo-5:6:5':6'-dibenzo-1:4:1':2'-tetrahydro-1:2:3':4'-quinazolinoquinazoline- $\beta\beta$ -dinaphthyl (II), m.p. 206–207° (acetate, m.p. 160–190°; hydrochloride, m.p. 308–310°; nitrite, m.p. 259°; picrate, m.p. 269–270°; Ac derivative, m.p. 245.5°), results. (II) is also obtained by heating (I) and $C(N \cdot C_{10}H_7 \cdot \beta)_2$ (III), which indicates that (II) probably arises in the original reaction by way of $CS(NH \cdot C_{10}H_7 \cdot \beta)_2$, which yields (III) by loss of H_2S . (I) in boiling AcOH $\cdot HCl$ gives $\beta \cdot C_{10}H_7 \cdot NH_2$ and 2-thio-2:4-diketo-5:6-



benzo-1:2:3:4-tetrahydroquinazoline (IV), m.p. > 350°; at 220°, however, S is lost and 2:4-diketo-5:6-benzo-1:2:3:4-tetrahydroquinazoline (V), m.p. 342°, is formed. (II) with KOH-EtOH at 160° affords the 4- β -naphthyl of (V), m.p. 301.5–302° (acetate, m.p. 301.5–302°; hydrochloride, m.p. 258–285°), which with conc. HCl at 200° gives (IV). (IV) and PCl_5 when heated yield 2:4-dichloro-5:6-benzoquinazoline, m.p. 184°, showing that (IV) can exist in the enolic form. That $\alpha \cdot C_{10}H_7 \cdot NH_2$ and other primary bases do not react with $CS(NH_2)_2$ in the above manner emphasises the reactivity of the α -H atom adjacent to the NH grouping in $\beta \cdot C_{10}H_7 \cdot NH_2$.

R. F. P.

Synthetic nucleosides. V. Theophylline-d-allomethyloside. P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1937, 117, 37–43).—d-Allomethylose with $Ac_2O \cdot C_5H_5N$ yields its Ac_4 derivative, m.p. 109–110°, $[\alpha]_D^{25} +10.4^\circ$, converted by HBr-AcOH into acetobromoallomethylose, which when heated (95–100°; 4 hr.) with Ag theophylline in PhMe gives theophyllinetriacetate-d-allomethyloside (I), m.p. 217–218°, $[\alpha]_D^{25} +12.5^\circ$ in MeOH, as an additive compound, m.p. 140°, $[\alpha]_D^{25} +11.0^\circ$ in MeOH, with 1 PhMe. $Ba(OMe)_2 \cdot MeOH \cdot H_2O$ hydrolyses (I) to theophylline-d-allomethyloside, m.p. 167–168°, $[\alpha]_D^{25} -21.9^\circ$ in H_2O , -6.5° in EtOH, the rate of hydrolysis of which in 0.1N-HCl at 100° is recorded.

H. G. M.

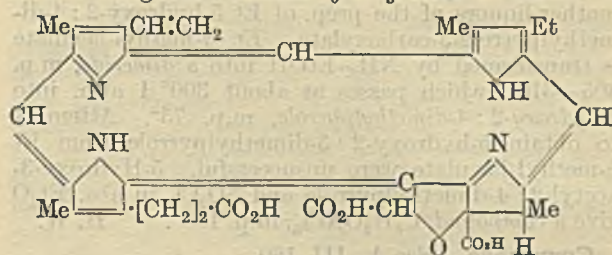
Production of tetrazoles of the camphor group and products therefrom.—See B., 1937, 289.

Preparation of purines and pyrimidines from nucleic acid. G. HUNTER and I. HLYNKA (Biochem. J., 1937, 31, 486–487).—Existing methods are shortened by using the difference in solubilities of the hydrochlorides of guanine and adenine on the one hand and of cytosine hydrochloride and uracil on the other. Separation of all four pure substances from nucleic acid is thus effected without intermediate formation of Cu or Ag salts.

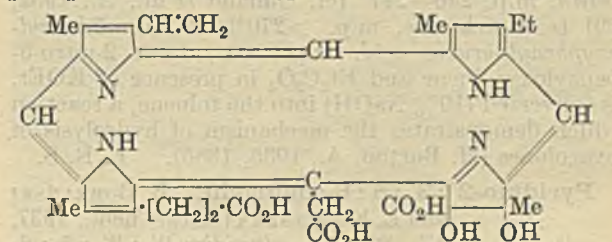
P. W. C.

Chlorophyll. LXXVI. Dihydroxychlorins and dihydroxyphorbides. H. FISCHER and W. LAUTSCH (Annalen, 1937, 528, 247–264).—Oxidation of phæophorbide-a in $C_5H_5N \cdot EtOH$ by Ag_2O [at room temp. gives purpurin 7 (isolated at the Me_3

ester), to which the following, modified constitution is now assigned. Chlorin- e_6 Me_3 ester is converted



by Ag_2O in C_5H_5N -dioxan-MeOH into dihydroxy-chlorin- e_6 Me_3 ester (I), m.p. 114°. Similarly meso-chlorin- e_6 Me_3 ester yields dihydroxymeso-chlorin Me_3 ester and D.E.E.-chlorin- e_6 Me_3 ester gives D.E.E.-dihydroxychlorin- e_6 Me_3 ester. These derivatives of chlorin- e_6 are decarboxylated by Na_2CO_3 in boiling C_5H_5N to the corresponding dihydroxyphæophorbide-a Me esters. (I) is also obtained from pyrophæophorbide-a and Ag_2O . Analytical and spectro-



scopic data are in harmony with the above constitution. ψ -Chlorin- p_6 Me_2 ester is oxidised to dihydroxy- ψ -chlorin- p_6 Me_3 ester, m.p. 120°, and chlorin- p_6 Me_3 ester to dihydroxychlorin- p_6 Me_3 ester, m.p. 118°, converted into chlorin- p_6 by catalytic hydrogenation or treatment with Na_2CO_3 in boiling C_5H_5N .

H. W.

Chlorophyll. LXXVII. Partial synthesis of methylphæophorbide-a and -b. H. FISCHER and W. LAUTSCH (Annalen, 1937, 528, 265–275).—Short, energetic treatment of chlorin- e_6 Me_3 ester (I) in C_5H_5N with 10% KOH-MeOH in N_2 gives methylphæophorbide-a (II), m.p. 236°, identical with that derived from chlorophyll except in respect of $[\alpha]$; this is probably due to the intermediate production of an enolic form. (II) is re-converted by CH_2N_2 -MeOH into (I). (II) is decarbomethoxylated in boiling C_5H_5N and then converted by CH_2N_2 in Et_2O into pyrophæophorbide-a Me ester, m.p. 230°, $[\alpha]_{590-720}^{25} -468^\circ$, against -352° as max. val. for the natural material. Similarly DEE-chlorin- e_6 Me_3 ester is smoothly transformed into DEE-methylphæophorbide-a, m.p. 233°, $[\alpha]_{590-720}^{25} -235^\circ$. Analogously, rhodin- g_7 Me_3 ester affords methylphæophorbide-b, m.p. (indef.) 261°, $[\alpha]_{590-720}^{25} -277^\circ$ (natural product, -128°), whence pyrophæophorbide-b Me ester, $[\alpha]_{590-720}^{25} -562^\circ$. An explanation in the discrepancies of $[\alpha]$ is difficult since, in this series, inactive materials have been isolated which afford inactive derivatives convertible by further treatment into active products.

[With H. HABERLAND.] Oxidation of opsopyrrole-carboxylic acid by H_2O_2 in C_5H_5N gives a compound, $C_8H_{11}O_3N$, m.p. 185–186°, and possibly two further

isomerides. 5-Hydroxy-2:4-dimethylpyrrole-3-carboxylamide, m.p. 217—218°, is obtained from the mother-liquors of the prep. of Et 5-hydroxy-2:4-dimethylpyrrole-3-carboxylate. Et α -methyl-lævulate is transformed by NH_3 -EtOH into a dimeride, m.p. 305—310°, which passes at about 300°/1 atm. into 5-hydroxy-2:4-dimethylpyrrole, m.p. 75°. Attempts to obtain 5-hydroxy-2:3-dimethylpyrrole from Et β -methyl-lævulate were unsuccessful. 5-Hydroxy-3-acetyl-2:4-dimethylpyrrole and SO_2Cl_2 in abs. Et_2O give a compound, $\text{C}_8\text{H}_4\text{ONCl}_3$, m.p. 188°. H. W.

Cozymase.—See A., III, 180.

5-Furfuryl-5-isopropylbarbituric acid.—See B., 1937, 290.

Alkaline hydrolysis of the azlactones derived from certain o-nitrobenzaldehydes. Formation of isatins. H. BURTON and J. L. STOVES (J.C.S., 1937, 402—404).—5-Keto-2-phenyl-4-(2'-nitro-4'-acetoxy-3'-methoxybenzylidene)-4:5-dihydro-oxazole is hydrolysed (10% NaOH) to 6-hydroxy-7-methoxyisatin, m.p. 246—247° (cf. Gulland *et al.*, A., 1932, 69) (semicarbazone, m.p. >270°). 2-Nitro-5-benzoyloxyphenylpyruvic acid, m.p. 103°, from 2-nitro-5-benzoyloxytoluene and $\text{Et}_2\text{C}_2\text{O}_4$ in presence of KOEt, is converted (10% NaOH) into the toluene, a reaction which demonstrates the mechanism of hydrolysis of oxazolones (cf. Burton, A., 1935, 1385). F. R. S.

Pyridino-2':3':5:6-coumarin. B. BOBRANŃSKI and L. KOCHANŃSKA (Rocz. Chem., 1937, 17, 30—32).—Pyridino-2':3':5:6-coumarin, m.p. 187°, is prepared from 7-hydroxyquinoline, $\text{CH}_2(\text{CO}_2\text{H})_2$, and H_2SO_4 (100°; 2 hr.), or from 7-hydroxy-8-aldehydequinoline, NaOAc, and Ac_2O (180°; 2 hr.). R. T.

Preparation and properties of thiazole compounds. H. ERLÉNMEYER and H. VON MEYENBURG (Helv. Chim. Acta, 1937, 20, 204—206).—Et chloroformylacetate is converted by $\text{HCS}\cdot\text{NH}_2$ into Et thiazole-5-carboxylate, b.p. 99—103°/11 mm., hydrolysed to thiazole-5-carboxylic acid (I), m.p. 196—197° (corr.) (Na salt). Analogously, Et_2 chloro-oxaloacetate affords Et_2 thiazole-4:5-dicarboxylate, b.p. 175°/12 mm., whence thiazole-4:5-dicarboxylic acid (II), decomp. 177° with formation of (I) [Na H salt (+1H₂O); Ba salt]. (II) is converted by SOCl_2 followed by $\text{NHEt}_2\cdot\text{HCl}$ at 160° into thiazole-4:5-dicarboxybisdiethylamide (III), m.p. 44° (corr.). Thiazole-5-carboxydiethylamide (IV), b.p. 152°/11 mm., m.p. 28°, is obtained analogously from (I) or from (II) after prolonged boiling with Ac_2O . The physiological properties of (III) and (IV) are described. H. W.

Aneurin. VII. Synthesis of aneurin. A. R. TODD and F. BERGEL (J.C.S., 1937, 364—367).—Acetamidine and $\text{OMe}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ in EtOH give Et α -cyano- β -acetamidinoacrylate (?), m.p. 108—110°, hydrolysed (NaOH) to 4-hydroxy-5-cyano-2-methylpyrimidine, m.p. 233—235°, which with POCl_3 forms the 4-Cl-compound, m.p. 63—64°, aminated to the 4-NH₂-derivative (I), m.p. 249° (cf. Grewe, A., 1936, 1566). Acetamidine hydrochloride and Et ethoxymethylenemalonate yield Et 4-hydroxy-

2-methylpyrimidine-5-carboxylate, m.p. 191°, which is converted through the Cl-compound into the 4-NH₂-derivative, m.p. 120°. The NH₂-ester with aq. NH_3 forms 4-amino-2-methylpyrimidine-5-carboxylamide, m.p. 264—265°, which with POCl_3 affords (I). (I) is reduced to 4-amino-5-aminomethyl-2-methylpyrimidine hydrochloride, which with HCS_2K gives 4-amino-5-thioformamidomethyl-2-methylpyrimidine, m.p. 187° (decomp.). Condensation of the thioformyl derivative with Me α -chloro- γ -acetoxypropyl ketone followed by HCl leads to aneurin chloride which is identical with the natural compound. The difference in m.p. between synthetic and natural specimens is due to dimorphism. F. R. S.

Spinazine, $\text{C}_9\text{H}_{14}\text{O}_4\text{N}_4$, decomp. 263—267°, from *Acanthias vulgaris*.—See A., III, 167.

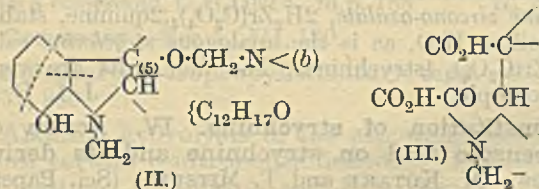
Condensations of indoles with aldehydes and secondary amines. I. New synthesis of gramine. H. KÜHN and O. STEIN (Ber., 1937, 70, [B], 567—569).—3-Dimethylaminomethylindole (gramine) is quantitatively obtained from indole, NHMe_2 , and CH_2O in AcOH at room temp. In alkaline solution the condensation is less complete and an unidentified colourless oil is also produced. 3-Diethylaminomethylindole, m.p. 165° (picrate, m.p. 124°), and 3-1'-piperidinomethylindole, m.p. 161°, are obtained similarly. H. W.

Optical rotation and refractivity of nicotine and nicotine sulphate in dilute aqueous solution.—See A., I, 169.

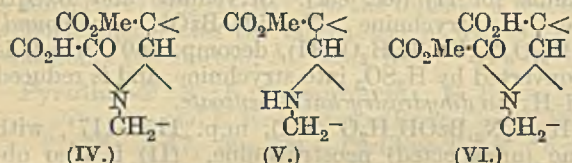
Constituents of the bark of *Lunasia costulata* (Miq.). H. DIETERLE and H. BEYL (Arch. Pharm., 1937, 275, 174—191).—This bark contains (a) 0.48% of tannins, (b) an oil, d 0.9506, acid val. 62.32, sap. val. 164, ester val. 101.7, I val. 118.5, which gives stearic (5.65), palmitic (13.76), oleic (60.38), and linolenic acid (15.66%), and (c) 0.083% of alkaloids, including lunacrine (I) (0.068%), lunasin, $\text{C}_{16}\text{H}_{21}\text{O}_5\text{N}$, m.p. 188° (0.009), and lunacridine, $\text{C}_{18}\text{H}_{15}\text{O}_4\text{N}$, m.p. 230—231° (0.0003%). (I), $\text{CH}_2\text{O}_2\cdot\text{C}_{13}\text{H}_{12}(\text{OMe})\cdot\text{NMe}$, + H_2O , m.p. 95—96°, (anhyd.) 115—116°, $[\alpha]$ 0 (hydrochloride, m.p. 163—164°; hydrobromide, m.p. 170—171°; hydriodide, m.p. 196—197°; picrate, m.p. 208°; aurichloride, m.p. 176—177°), gives a methiodide, m.p. 130—131°, which with Ag_2O gives a substance, $\text{C}_{16}\text{H}_{20}\text{O}_3\text{N}$, m.p. 85—86°, insol. in dil. HCl, also obtained from the methosulphate by hot 30% KOH. (I) is very stable; 30% H_2O_2 gives a cryst. product. Photomicrographs of the alkaloids and bark are given. R. S. C.

Properties of the ecgonines and their esters. I, II. A. W. K. DE JONG (Rec. trav. chim., 1937, 56, 186—197, 198—201).—I. $[\alpha]$ of *l*-ecgonine in different solutions is discussed, and an optical method for its determination in admixture with a lævotatory compound, not affected by boiling 20% KOH, is described. The hydrolysis of ecgonine esters with HCl first yields ecgonine, which is then partly transformed into ecgonidine (I); this latter change also occurs with 20% KOH. At room temp. esters of *l*-ecgonine are partly transformed by alkali in EtOH or COMe_2 into *d*-*p*-ecgonine (stable to conc. HCl). *l*-Cocaine at 115—120° yields *d*-ecgonine Me

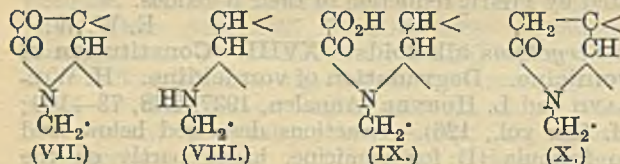
the CO_2H attached to $\text{C}_{(5)}$ and the ready loss of this CO_2H by the action of HCl or heat. Improved CrO_3 -oxidation of vomitidine (II) gives, by fission at the dotted lines, the acid (III), new formula $\text{C}_{19}\text{H}_{24}\text{O}_7\text{N}_2 + 2\text{H}_2\text{O}$ (lost only with decomp.), m.p. 219–220° (decomp.) (slow heating), stable to conc. HNO_3 , Br , $\text{Ca}(\text{OCl})_2$, H_2O_2 , and alkali, hydrogenated with loss of CO_2 , and giving no CO reactions. When evaporated with KOH-MeOH at 120°, (III) gives HCO_2H and $\text{H}_2\text{C}_2\text{O}_4$. With $\text{CH}_3\text{N}_2\text{-MeOH}$ (III) gives



the *Me* ester, m.p. 235–236° (decomp.), sublimes at 180°/high vac., stable to Ac_2O , hydrogenated (PtO_2) to a substance, $\text{C}_{19}\text{H}_{26}\text{O}_4\text{N}_2(\text{OMe})_2$, m.p. 136° (presumably by the reaction $\text{C}_{(5)}\cdot\text{O}\cdot\text{C} \rightarrow \text{CH}=\text{CH}$), and hydrolysed by N-KOH-MeOH to the *H Me* ester (IV), $\text{C}_{19}\text{H}_{23}\text{O}_6\text{N}_2\cdot\text{OMe}$, m.p. 255° (decomp.) (hydrochloride, decomp. 214°). At 235–240°/high



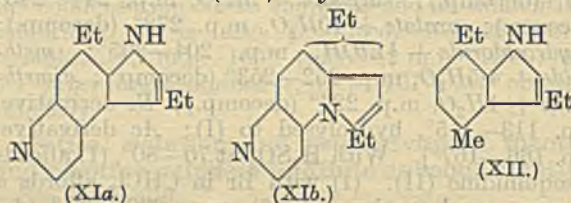
vac. (IV) gives CO_2 , CO , and a base (V), $\text{C}_{18}\text{H}_{26}\text{O}_4\text{N}_2$, m.p. 159–160°. HCl-MeOH and (III) give the *H Me* ester (VI), sinters at 190°, decomp. 276° [hydrochloride, m.p. 206° (decomp.)], which at 200°/high vac. gives CO_2 and a base (VII), $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_2$, m.p. 282–284° (decomp. from 250°). At 200°/high vac.



(III) gives 1.4 mols. of CO_2 , CO , 20% of (VII), and 15% of a dibasic substance (VIII), $\text{C}_{16}\text{H}_{24}\text{O}_2\text{N}_2$, m.p. 146° (100° after being kept in air) [1 active H ; hydrochloride, m.p. 278° (decomp. from 250°); *Ac* derivative, m.p. 223–225° (decomp.)]; with MeI gives the (?) dihydriodide, $\text{C}_{17}\text{H}_{28}\text{O}_2\text{N}_2\text{I}_2$, (α) NHMeI . . .

$\cdot\text{O}\cdot\text{CH}_2\cdot\text{N}(b)\text{HI}$, m.p. 259° (decomp.). (VIII) is obtained in 75% yield with CO_2 and CO from (III) and 2N-HCl at 155°, is hydrogenated (PtO_2 ; saturation of the ethylenic linking) in H_2O to a base, $\text{C}_{16}\text{H}_{26}\text{O}_2\text{N}_2 + \text{H}_2\text{O}$, m.p. 154–155°, stable to $\text{H}_2\text{-Pt}$ at 120°/100 atm., is reduced by HI -red or -yellow P to a base, $\text{C}_{16}\text{H}_{26}\text{O}_2\text{N}_2$, m.p. 167°, by fission of the $\text{O}_{(4)}$ ring, and resists SOCl_2 and PCl_5 . (VII) does not react with MeI , is hydrogenated (PtO_2 ; saturation of the ethylenic linking, $\text{C}\cdot\text{O}\cdot\text{C} \rightarrow \text{CH}=\text{CH}$, $\text{C}\cdot\text{O}\cdot\text{C} \rightarrow \text{CH}=\text{CH}$, and $\text{CO} \rightarrow \text{CH}_2$) to a base, $\text{C}_{18}\text{H}_{30}\text{O}_3\text{N}_2$, m.p. 197° (methiodide, m.p. 262°, stable to alkali), with hot 10% KOH-MeOH gives the acid

(IX), $\text{C}_{18}\text{H}_{24}\text{O}_5\text{N}_2 + 5\text{H}_2\text{O}$, m.p. 214° (decomp.) (<50% yield) (*Me* ester, m.p. 157°), and gives a 2:4-dinitrophenylhydrazone, m.p. >330°, decomp. from 250°. The hydrazone, $+1.5\text{H}_2\text{O}$, m.p. 251° (decomp.), of (VII) with HNO_2 gives N_2O and regenerates (VII) and with hot NaOEt-EtOH affords the deoxo-base (X), $\text{C}_{18}\text{H}_{24}\text{O}_3\text{N}_2 + 0.5\text{H}_2\text{O}$, m.p. 186° (decomp.), hygroscopic, stable to 10% KOH-MeOH , reduced ($\text{H}_2\text{-PtO}_2$) in H_2O mainly to a substance, $\text{C}_{18}\text{H}_{28}\text{ON}_2$, an oil [hydrochloride, $+0.5\text{H}_2\text{O}$, m.p. 262° (decomp.; sinters at 250°); methiodide, cryst.]. (VIII) is dehydrogenated by Pd at 145–150° (later at 230°), giving vomipyrine (XI), $\text{C}_{15}\text{H}_{16}\text{N}_2$, m.p. 105–106° (yellow hydrochloride), an oily base, (?) $\text{C}_{14}\text{H}_{14}\text{N}_2$, b.p. 164–165°/high vac. (yellow hydrochloride, sinters at 220°, m.p. 240°, loses HCl at 80°), and a base (XII), $\text{C}_{13}\text{H}_{17}\text{N}$, b.p. 150–160°/12 mm. (XI) is unchanged by $\text{H}_2\text{-Pd-C}$, but with $\text{Na-C}_5\text{H}_{11}\cdot\text{OH}$ gives a H_4 -base, $\text{C}_{15}\text{H}_{20}\text{N}_2$ [hydrochloride, m.p. 221° (decomp.; sinters at 200°)]. The last four bases give the pine shaving reaction. (XI) is probably (XIa); (XIb) would account for the coloured salts, but is less probable for other reasons. (XII) may be as shown.



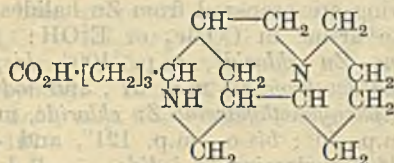
R. S. C.

α - and β -Hydroxylaudanosines. II. Products of exhaustive methylation. F. E. KING and P. L'ECUYER (J.C.S., 1937, 427–432).—Degradation of α -hydroxylaudanosine methiodide, m.p. 168° (efferv.), and methochloride, m.p. 165–166° (efferv.), and the β -methiodide, m.p. 223–225°, and methochloride, m.p. 217–218° (efferv.), with NaOH or Ag_2O gives 4:5-dimethoxy-2-vinylbenzylidimethylamine (I), b.p. 128°/2 mm. [picrate, m.p. 158–159°; methiodide, m.p. 197–198°; methochloride, m.p. 218° (efferv.)], which with dil. acid yields veratraldehyde (2:4-dinitrophenylhydrazone, m.p. 253–255°). Catalytic reduction of (I) affords 4:5-dimethoxy-2-ethylbenzylidimethylamine (II), b.p. 108°/0.06 mm. [picrate, m.p. 110–111°; methiodide, m.p. 209°; methochloride ($+ \text{H}_2\text{O}$) (III), m.p. 150–151°]. Degradation of (III) by Emde's method gives 4-methyl-5-ethylveratrole, b.p. 105°/5 mm., demethylated to 4-methyl-5-ethylpyrocatechol (*di-p*-nitrobenzoate, m.p. 124–125°), also obtained by synthesis from 4:5-dimethoxy-2-methylacetophenone. 5-Nitro-4-ethylveratrole, m.p. 54–54.5°, prepared by nitration, is reduced to the 5-amino-compound, m.p. 63° (*Ac* derivative, m.p. 147°), which yields the 5-CN-derivative, m.p. 60°, reduced (Na-EtOH) to (II) [picrolonate, m.p. about 235° (decomp.)]. The methiodides of synthetic and natural specimens of (II) are identical. (III) on distillation/high vac. gives 4:5-dimethoxy-2-ethylbenzyl chloride, b.p. 128°/1 mm., m.p. 40°, also obtained from 4-ethylveratrole and CH_2O ; the chloride with NHMe_2 forms (II).

F. R. S.

Lupin alkaloids. XIII. Fission of the piperidone ring of lupanine by fuming hydrochloric

acid. E. HOFFMANN, F. W. HOLSCHNEIDER, and K. WINTERFELD (Arch. Pharm., 1937, 275, 65—66; cf. this vol., 125).—The lactam nature of lupanine is confirmed by fission by conc. HCl at 150° to the acid (platinichloride, +H₂O, decomp. 245°, of the *Et* ester), having the structure



R. S. C.

Alkaloids of ergot. VIII. New alkaloids of ergot: ergosine and ergosinine. S. SMITH and G. M. TMMIS (J.C.S., 1937, 396—401).—Ergosinine, (I), C₃₀H₃₇O₅N₅ (+0.5MeOH), m.p. 220° (decomp.), (hydrochloride, decomp. about 206°) (cf. A., 1936, 351, 1131), is degraded by hydrolysis and pyrolysis to lysergic acid, NH₃, ergine, *d*-proline, *l*-leucine, and AcCO₂H. (I) is converted (KOH-EtOH) into ergosine (II) [hydrochloride, m.p. 235° (decomp.); hydrobromide, decomp. 230°; nitrate, decomp. 215°; methiodide, decomp. 215°]. (I) and (II) form a mol. compound, m.p. 200° (decomp.), [α]_D²⁰_{CHCl₃} +164° in CHCl₃. (I), heated under reduced pressure, gives with other cryst. products *l*-leucyl-*d*-proline lactam, m.p. 148°, [α]_D²⁰_{CHCl₃} +105° in H₂O. (I) and (II) differ as regards [α] and their physiological activity in the same sense as do, e.g., ergotamine and ergotamine.

F. R. S.

Synthesis of substances related to lysergic acid. W. A. JACOBS and R. G. GOULD, jun. (Science, 1937, 85, 248—249; cf. A., 1936, 1277).—Reduction of naphthostyryl with Na in BuOH yields 3:4-trimethyleneindole (I), with 8-amino-1-hydroxymethyl-1:2:3:4-tetrahydronaphthalene as by-product. (I) exhibits the usual indole reactions, but not the characteristic Keller reaction of the ergot alkaloids.

A nearer approach to the synthesis of lysergic acid (II) has been achieved as follows. 3:1-NH₂-C₁₀H₆-CO₂H by the Skraup reaction gives the corresponding β-naphthoquinolinecarboxylic acid, which is nitrated to a nitro-β-naphthoquinoline carboxylic acid. After reduction of the NO₂ to NH₂, lactamisation occurred forming the substance (III). Reduction of (III) with Na and BuOH yields a mixture which gives colour reactions closely approaching those characteristic of (II) and its derivatives.

L. S. T.

Derivatives of berbine. IV. Hydrogenation with amalgamated zinc and an addition of amalgamated cadmium. W. AWE and H. UNGER (Ber., 1937, 70, [B], 472—478).—The use of Cd-Hg in the Clemmensen reaction offers no advantage over that of Zn-Hg but mixtures of Zn-Hg and Cd-Hg (3:1) allow the change to proceed much more rapidly and with much better utilisation of H. Conc. HCl can be replaced by 30% AcOH containing 2N-H₂SO₄. The method is particularly suited for the conversion of isoquinoline bases into their H₄-derivatives. The following examples are cited: berberinium H sul-

phate to 16:17-dihydrodeoxyberberine; palmatinium iodide to 16:17-dihydrodeoxypalmatine; 9-benzyldeoxyberberine to 11:12-dimethoxy-2:3-methylene-dioxy-9-benzylberbine, m.p. 165—166°, and its *ψ*-form, m.p. 146°; 9-*o*-tolyl- and 9-*o*-methoxyphenyldeoxyberberine to 11:12-dimethoxy-2:3-methylene-dioxy-9-*o*-tolyl- and 9-*o*-methoxyphenylberbine, respectively; 9-phenyldeoxypalmatine hydrobromide to 2:3:11:12-tetramethoxy-9-phenylberbine, m.p. 172°, and (?) 9-phenyl-16:17-dihydrodeoxypalmatine, m.p. 139—140°; papaverine methiodide to *dl*-laudan- osine. Codeine appears largely unaffected. H. W.

Alkaloid from Chinese hanfangchi. S. K. LIU, C. MA, and S. Y. LI (Pharm. Chem. Res. Rept. [China], 1935, 1, No. 1, 1—11, 13—28).—Extraction with AcOH or EtOH and recrystallisation of the phosphate yields an alkaloid, m.p. 215—217°, [α]_D²⁰_{CHCl₃} +280.8° in CHCl₃, containing 1 double linking, 1:CO, 2 OMe, and 1 NMe.

CH. ABS. (r)

Alkaloid from Japanese hanfangchi. S. K. LIU, C. MA, S. Y. LI, and C. F. LO (Pharm. Chem. Res. Repts. [China], 1935, 1, No. 1, 29—35, 37—49).—Extraction with EtOH followed by recrystallisation of the hydrochloride yields an alkaloid, C₁₉H₂₃O₄N, m.p. 160—163°, [α]_D²⁰_{CHCl₃} —66° in CHCl₃ (hydrochloride, m.p. 235—239°), which contains 1 double linking, 1:CO, 1 phenolic OH, 2 OMe, and 1 NMe.

CH. ABS. (r)

Alkaloids of Sinomenum and Cocculus. XLIV. Phenolic alkaloid of C. trilobus, D.C. 3. Constitution of normenisarine. XLV. Review on the biscoclaurine alkaloids. Consideration from the stereochemical and biogenetic viewpoint. H. KONDO and M. TOMITA (J. Pharm. Soc. Japan, 1935, 55, 911—913, 914—933).—XLIV. Normenisarine, C₃₂H₂₂(OMe)₂(O⁺)₃(NMe)(N), m.p. 223°, yields menisarine, C₃₃H₂₅N₂O₃(OMe)₃, m.p. 164°, on methylation.

XLV. A review.

CH. ABS. (r)

Rotatory power of some alkaloids. C. LORMAND and P. GESTEAU (XIV Congr. Chim. ind. Paris, 1934, Comm. 2, 3 pp.; Chem. Zentr., 1936, i, 3145).—[α]_D²⁰ for λ 5893, 5780, 5460, 4358, and 4046 are recorded for cocaine hydrochloride, codeine, heroine hydrochloride, picrotoxin, emetine hydrochloride, pilocarpine hydrochloride and nitrate, scopolamine hydrobromide, and eserine and its salicylate.

H. N. R.

Arsinic acids. F. F. BLICKE and G. L. WEBSTER (J. Amer. Chem. Soc., 1937, 59, 534—537).—PhAsO (in aq. NaOH) and *m*-NO₂-C₆H₄-N₂Cl (neutralised) give *m*-nitrodiphenylarsinic acid, m.p. 154—155°, reduced (FeSO₄, aq. NaOH) to the *m*-NH₂-acid, m.p. 210—212°, which is converted (diazo-method) into the *m*-OH-acid, m.p. 230—232°, and thence by Me₂SO₄ + aq. NaOH into *m*-methoxydiphenylarsinic acid, m.p. 120—121°. *o*-Hydroxy-, m.p. 221—223°, and *o*-methoxy-, m.p. 187—188°, -diphenylarsinic acids are similarly prepared. *p*-Bromodiphenylarsinic acid, m.p. 184—185°, is obtained from PhAsO and *p*-C₆H₄Br-N₂Cl. *p*-Nitrodiphenylarsinic acid (in conc. H₂SO₄) with HNO₃ (d 1.42) + conc. H₂SO₄ at 0—3° give the 3:4'-(NO₂)₂-acid, m.p. 230—232°.

reduced (method: A., 1934, 312) to the 3:4'-(NH₂)₂-acid, m.p. 176—178°, which is converted (diazomethod) into 3:4'-dihydroxydiphenylarsinic acid, m.p. 210—211°. 3:3'-Dinitro-4-hydroxydiphenylarsinic acid, m.p. 195—196°, is obtained by similar nitration of *p*-hydroxydiphenylarsinic acid. 3-Nitro-4-methoxyphenylarsine oxide, m.p. 247—248° (decomp.), and MeI in aq. MeOH-NaOH give 3-nitro-4-methoxyphenylmethylarsinic acid, m.p. 216—217°. 3-Amino-4-hydroxyphenylmethylarsinic acid, m.p. 233—234° (lit. 206—207°), is prepared by reduction (FeSO₄, aq. NaOH) of the 3-NO₂-acid (Berthelm, A., 1915, 1, 331). The prep. of *p*-C₆H₄Br·AsO₃H₂ is improved. The following are obtained from the requisite acids by the usual methods: *p*-NO₂-C₆H₄·AsCl₂, which with piperidine *N*-pentamethylenedithiocarbamate gives *p*-nitrophenylarsylene *N*-pentamethylenedithiocarbamate, m.p. 177—178°; *o*-nitrodiphenyliodoarsine, m.p. 113—114°; *o*- (I) and *m*-, m.p. 173—175°, aminodiphenylchloroarsine hydrochlorides; 3-amino-4-hydroxyphenylmethyl-chloroarsine hydrochloride, m.p. 178—180°, and -iodoarsine hydriodide, m.p. 136—137°; *o*-methoxydiphenyliodoarsine, m.p. 68—69°; *p*-OMe·C₆H₄·AsCl₂, m.p. 49—50°. (I) and aq. NH₃ give 2:2'-diaminotetraphenylarsyl oxide, the Ac₂ derivative (+1.5AcOH), m.p. 180—181°, of which with aq. HI affords *o*-acetamidodiphenyliodoarsine, m.p. 147—148° (the *m*-isomeric, m.p. 146—147°, is similarly prepared). *o*-OH·C₆H₄·AsCl₂ and aq. Na₂CO₃ give (cf. Kalb, A., 1921, i, 375) an anhydride, m.p. 181—182°, of *o*-OH·C₆H₄·As(OH)₂. H. B.

Synthesis of *p*-benzylthiolbenzenearsinic acid. T. TAKAHASHI (J. Pharm. Soc. Japan, 1935, 55, 875—879).—*p*-NO₂-C₆H₄·SH, m.p. 77°, from *p*-C₆H₄Cl·NO₂ with KOH and H₂S, yields, with KOH and CH₂PhCl, 4-nitrophenyl benzyl sulphide, m.p. 123°, reduced to 4-aminophenyl benzyl sulphide (hydrochloride, m.p. 256°; Ac derivative, m.p. 133° and 105°; Bz derivative, m.p. 182°), which, on diazotisation and treatment with Na₃AsO₃, yields *p*-benzylthiolphenylarsinic acid, decomp. 250°.

CH. ABS. (r)

Compounds formed by mercury salts with tertiary arsines. J. J. ANDERSON and G. J. BURROWS (J. Proc. Roy. Soc. New South Wales, 1936, 70, 63—68).—The following are prepared from Hg^{II} halides and AsPh₂Me in boiling EtOH: diphenylmethylarsine Hg^{II} chloride, m.p. 186°, bromide, m.p. 142°, and iodide, m.p. 116°; below 50° the reaction products are bisdiphenylmethylarsine Hg^{II} chloride, m.p. 131°, bromide, m.p. 100.5°, and iodide, m.p. 83°. AsPhMe₂ and Hg^{II} halides in boiling EtOH yield phenyldimethylarsine Hg^{II} chloride, m.p. 201°, bromide, m.p. 171°, and iodide, m.p. 144°, and below 50°, bisphenyldimethylarsine Hg^{II} chloride, bromide, m.p. 115°, and iodide, m.p. 104°. J. D. R.

Co-ordination compounds of cadmium with tertiary arsines. G. J. BURROWS and A. LENCH (J. Proc. Roy. Soc. New South Wales, 1936, 70, 218—221).—The following are prepared by interaction of Cd halide with the appropriate arsine in hot EtOH: phenyldimethylarsine Cd chloride, m.p. 220°, bromide, m.p. 186°, iodide, m.p. 108°; diphenylmethylarsine Cd chloride, m.p. 292°, bromide, m.p. 257°; bisdi-

phenylmethylarsine Cd chloride, m.p. 100°; bis-*o*-, m.p. 187°, and -*p*-, m.p. 126°, -tolylldimethylarsine Cd iodide. J. D. R.

Derivatives of zinc halides with tertiary arsines. G. J. BURROWS and A. LENCH (J. Proc. Roy. Soc. New South Wales, 1936, 70, 222—224).—The following are prepared from Zn halides and the appropriate arsine in COMe₂ or EtOH: phenyldimethylarsine Zn chloride, m.p. 100°, bisphenyldimethylarsine Zn bromide, m.p. 67°, and iodide, m.p. 92°; bis-diphenylmethylarsine Zn chloride, m.p. 128°, bromide, m.p. 76°; bis-*o*-, m.p. 121°, and -*p*-, m.p. 115°, -tolylldimethylarsine Zn iodide. J. D. R.

Preparation of camphor-10-dichloroarsine from camphor-10-sulphinic acid. J. D. LOUDON (J.C.S., 1937, 391—392).—Camphor-10-sulphinic acid and AsCl₃ give camphor-10-dichloroarsine (I), m.p. 89—90°, also obtained from biscamphor-10-mercury and AsCl₃. (I) is hydrolysed (NaOH) to camphor-10-arsinous acid, m.p. 100° (decomp.), and oxidised (Cl₂ or H₂O₂) to the -arsinic acid, m.p. 210°. F. R. S.

Complex compounds formed by the reaction between phenyldichlorostibine and benzene-diazonium chloride. A. B. BRUKER (J. Gen. Chem. Russ., 1936, 6, 1823—1827).—Aq. PhN₂Cl, AcOH, and SbPhCl₂, or SbPh·OCl in AcOH, at 0°, yield the complex, PhN₂Cl·SbPhCl₂, decomp. at 58—60° to give SbPh₂Cl₃ and N₂. R. T.

Reaction of organic bismuth compounds with mercuric chloride. L. G. MAKAROVA (J. Gen. Chem. Russ., 1937, 7, 143—147). The following reactions are described: BiPh₃Cl₂ (I) + HgCl₂ + H₂O → HgPhCl (II) + BiOCl + 2C₆H₅ + Cl₂; (I) + 3HgCl₂ + H₂O → 3(II) + BiOCl + Cl₂ + 2HCl; BiPh₂Cl (III) + HgCl₂ + H₂O → (II) + BiOCl + C₆H₅ + HCl; (III) + 2HgCl₂ + H₂O → 2(II) + BiOCl + 2HCl. R. T.

Aromatic phosphorus halides and their suitability for the volumetric determination of water. J. LINDNER, W. WIRTH, and B. ZAUNBAUER (Monatsh., 1937, 70, 1—19; cf. A., 1931, 1257).—Further examination of P aryl halides does not lead to the discovery of a material more suitable than C₁₀H₇·POCl₂ (A., 1925, ii, 901) for the determination of H₂O by conversion into HCl, which is titrated. Ph₂, PCl₃, and AlCl₃ give *P* diphenyllyl dichloride (mixture of isomerides), transformed by Cl₂ in CCl₄ into *P* diphenyllyl tetrachloride, which with SO₂ affords the corresponding oxychloride, b.p. 220°/10—11 mm., m.p. 90° after softening at 70°. PPhCl₂, b.p. 221°/1 atm., m.p. -51°, best obtained from C₆H₆ and PCl₃ at 600°, is converted by Cl₂ in CCl₄ into PPhCl₄, m.p. 73°, and the compound, PPhCl₄·PCl₅, m.p. >200°, also obtained from PPhCl₂, PCl₃, and Cl₂ in CCl₄. Cl₂ and PPhCl₄ in CCl₄ yield the substance, PPhCl₄·Cl₂, which readily loses 2Cl. The analogous compound, PPhCl₄·Br₂, m.p. 134° (decomp.; sealed capillary), is more stable. The behaviour of the compounds when heated in air and the effects of light are described. H. W.

Structure of hypophosphorous acid. I. Reaction of aryldiazonium salts with hypophosphites. II. Reaction of arylhydrazines with

hypophosphites. III. Reaction of aryldiazonium salts with phosphorus trichloride and sodium diisopropyl phosphite. IV. Reaction of hypophosphites with alkyl halides. V. M. PLETZ (J. Gen. Chem. Russ., 1937, 7, 84—89, 90—92, 270—272, 273—276).—I. The following arylphosphinic acids have been prepared by the reaction NaH_2PO_2 (I) + $\text{R}\cdot\text{N}_2\text{Cl} \rightarrow [\text{H}_2\text{PO}\cdot\text{O}\cdot\text{N}_2\text{R}] \rightarrow \text{RH}_2\text{PO}_2 + \text{N}_2$: phenyl-, o-, m.p. 115°, and p-tolyl-, o-, m.p. 157°, and p-nitrophenyl-, m.p. 134°, α - and β -naphthylphosphinic acid, m.p. 175°, and diphenyldiphosphinic acid, m.p. 167°.

II. The following compounds are obtained from (I) and various hydrazines in aq. solution, in presence of CuSO_4 , by the reaction $\text{NHR}\cdot\text{NH}_2 + (\text{I}) \rightarrow \text{NHR}\cdot\text{NH}\cdot\text{PH}_2\cdot\text{O}$ (II) + NaOH ; (II) + $\text{O} \rightarrow \text{RH}_2\text{PO}_2 + \text{N}_2 + \text{H}_2\text{O}$: phenyl-, p-bromophenyl-, and p-nitrophenyl-phosphinic acid.

III. PCl_3 or NaPr_2PO_3 do not react with benzenediazonium compounds.

IV. (I) and EtBr or EtI in H_2O react as follows: $3(\text{I}) + 3\text{EtX} \rightarrow 3\text{NaX} + \text{PH}_2\text{Et} + 2\text{EtH}_2\text{PO}_2$. The reaction with $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ involves intermediate production of $\text{H}_2\text{PO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which readily eliminates CO_2 , to yield MeH_2PO_2 . R. T.

Review on the organic compounds of phosphorus. V. M. PLETZ (Uspechi Chim., 1935, 4, 573—609).—A comprehensive survey. In the presence of Cu , PhN_2Cl reacts with PCl_3 and PhPCl_2 to give PPhCl_4 and PPh_2Cl_3 , respectively. CH. ABS. (r)

(A) Structure of products of addition of mercury salts to unsaturated compounds by the arylation method. A. N. NESMEJANOV and R. C. FREIDLIN. (B) Reaction of diazomethane with β -bromomercuriethyl alcohol, and the structure of the products of addition of mercuric salts to olefines. R. C. FREIDLIN, A. N. NESMEJANOV, and F. A. TOKAREVA (J. Gen. Chem. Russ., 1937, 7, 43—50, 262—266).—(A) $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgBr}$ (I) in C_6H_6 and PhNCO yield β -bromomercuriethyl phenylcarbamate (II), m.p. 124—126° (decomp.). (I) in aq. alcoholic KOH and di-p-tolyldichlorostannane afford β -hydroxyethyl-p-tolylmercury (III), m.p. 52.5—53.5°. $\text{Hg}(\text{OAc})_2$ and cyclohexene (IV) in H_2O yield 2-acetomercuricyclohexanol, m.p. 112.5—113.5°, which reacts with SnPh_2Cl_2 (V) in $\text{EtOH}\cdot\text{KOH}$, at the b.p., to afford 2-phenylmercuricyclohexanol (VI), m.p. 101—102°. $\text{Hg}(\text{OAc})_2$ and (IV) in EtOH give 1-ethoxy-2-acetomercuricyclohexane, m.p. 76°, converted by boiling with NaOH and (V) in EtOH into *Hg phenyl 2-ethoxycyclohexyl* (VII). 1-Chloromercurimethyl-1:2-dihydrobenzofuran, NaOH , and (V) in EtOH , at the b.p., afford 1-phenylmercurimethyl-1:2-dihydrobenzofuran, m.p. 60—61°. This, similarly to (II), (III), (VI), and (VII), is decomposed by 15% HCl , with production of unsaturated hydrocarbon and Hg aryl chloride. The reactions support the structure given above for (I), rather than one involving residual valencies, of the type $\text{C}_2\text{H}_4\cdot\text{HgBrOH}$.

(B) (I) and CH_2N_2 in Et_2O yield β -bromomethylmercuriethyl alcohol, which decomposes at room temp. with production of C_2H_4 , Hg , bromomethylmercuric bromide (VIII), m.p. 124—125°, CH_2O , and N_2 . HgBr_2 and CH_2N_2 in Et_2O yield (VIII) and

Hg dibromodimethyl, m.p. 42—43°. (VIII) and aq. NaOH yield Hg , CH_2O , and HBr . R. T.

Lead organic compounds containing the carbethoxy-group. K. A. KOTSCHESCHKOV and A. P. ALEXANDROV (J. Gen. Chem. Russ., 1937, 7, 93—96).—K Et malonate in EtOH and PbPh_3Cl in COMe_2 yield *Et triphenylplumbyl malonate*, m.p. 159—160° (decomp.), converted by heating at 160—165° in vac. into *Et triphenylplumbiacetate*, m.p. 59—60°. K Et benzylmalonate similarly gives *Et triphenylplumbyl benzylmalonate*, m.p. 131—132° (decomp.), and *Et γ -phenyl- α -triphenylplumbibutrate*, m.p. 82—84°. R. T.

Reduction of organic mercury compounds by tin alkyl compounds, as a method of synthesis of hydroxy- and amino-aryl tin compounds. A. N. NESMEJANOV, K. A. KOTSCHESCHKOV, and V. P. PUZIREVA (J. Gen. Chem. Russ., 1937, 7, 118—121).—The following compounds have been prepared, by the reactions $\text{Sn}_2\text{Et}_6 + \text{RHgCl} \rightarrow \text{SnEt}_3\text{Cl} + \text{SnREt}_3 + \text{Hg}$; $\text{Sn}_2\text{Et}_6 + \text{HgR}_2 \rightarrow 2\text{SnREt}_3 + \text{Hg}$: SnPhEt_3 , p-dimethylaminophenyl- (I), b.p. 172—173°/3 mm., and o-hydroxyphenyl-triethylstannane, b.p. 197—200°/3 mm. (I) with HgCl_2 yields $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ and SnEt_3Cl , and with Br gives $p\text{-C}_6\text{H}_4\cdot\text{Br}\cdot\text{NMe}_2$ and SnEt_3Br . SnEt_2 yields SnEt_2Cl_2 and Hg with HgCl_2 , and SnPh_2Et_2 and Hg with HgPh_2 . R. T.

Relative reactivities of organometallic compounds. XV. Organoalkali compounds. H. GILMAN and R. V. YOUNG (J. Org. Chem., 1936, 1, 315—331).—The prep. of the compounds CPh:CM ($\text{M} = \text{MgBr}$, Li , Na , K , Rb , and Cs) in Et_2O is described, and the times required for reaction with PhCN under comparable conditions given, no significant reaction with Et_2O being observed. The reactivity of these compounds increases in the above order, which accords with the reactivity sequences obtained from the metalation of dibenzofuran (I) by EtM ($\text{M} = \text{Li}$, Na , and K) and the reaction with Bu^nCl of the benzophenone alkali compounds of K , Rb , and Cs . Further, EtLi in light petroleum at room temp. gives only monometalation of (I), whilst NaEt and in greater amounts KEt also give dimetalation. Na-K alloy reacts with $\text{CMc}_2\text{Ph}\cdot\text{OMe}$ giving CMc_2PhK , and similarly only organo-K compounds are obtained from $\text{CPh}_3\cdot\text{OEt}$, $\text{CHPh}_2\cdot\text{OMe}$, $(\text{CHPh}_2)_2$, and CHPh_3 . Only Na adds to $(\text{CPh}_2)_2$ giving $(\text{CNaPh}_2)_2$, but Na-K and Na-Rb alloys give the corresponding K and Rb compounds, respectively. 4-Dibenzofuryl-sodium and -potassium split Et_2O to an appreciable extent; they react more rapidly with PhF than with PhCl , and immediately with $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CN}$, but in the case of PhCl the Na - is more reactive than the K -compound. The reaction of CPh_3Li and CPh_2Na with PhCl and PhBr is also anomalous in that the Li - reacts more rapidly than the Na -compound, but with $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CN}$ the Na -compound is the more reactive. All the foregoing organoalkali compounds are satisfactorily carbonated at room temp. except the Li -compounds which are better carbonated at low temp. or with solid CO_2 . Conductivity results and electromotive series are

shown to be of limited use for predicting relative reactivities of organometallic compounds. H. G. M.

Organometallic compounds of styrene. G. F. WRIGHT (J. Org. Chem., 1936, 1, 457—463).—The reported prep. of *cis*- and *trans*-phenylbutadienes (A., 1931, 349) is not confirmed. *cis*- (I) and *trans*- β -bromostyrene (II) react with pure Mg (in absence of I and of O₂) to form, after an induction period, *cis*- and *trans*-Mg styryl bromide. The former with solid CO₂ gives 9% *trans*- and 19% *cis*-, and the latter 30% *trans*- and 20.5% *cis*-cinnamic acid, together with 3% and 11% *trans-trans*- $\alpha\delta$ -diphenylbuta- $\alpha\gamma$ -diene (III), respectively. The yield of 12% of *cis*-acid from the equilibrium mixture of (I) and (II) [largely (II)] shows that isomerisation has not occurred in the halide itself, but in the Mg compound. With MeCHO, both Mg derivatives give mixed isomeric methylstyrylcarbinols. With Mg and HgBr₂, the above equilibrium mixture yields styrylmercuric bromide, m.p. 202—203° (converted by I into β -iodostyrene). Either (I) or (II) with Li yields *Li styryl*, converted by solid CO₂ into a 4 : 1 mixture of *trans*-cinnamic and phenylpropionic acids, with (III). A new flask for the Grignard reaction, of inverted conical shape, is described. E. W. W.

Rhizopenin.—See A., III, 144.

Structure of proteins. Ox hæmoglobin, ovalbumin, ox fibrin, and gelatin.—See A., III, 168.

Quantitative organic micro-analysis. H. LIEB and A. SOLTYS (Mikrochem., Molisch Festschr., 1936, 290—300).—Points of technique as to wt. calibration, and the determination of C, H, N, halogens, Ac, and mol. wts. (Rast method) are discussed. J. S. A.

Pressure regulator for carbon and hydrogen determination. H. ROTH (Mikrochem., Molisch Festschr., 1936, 373—374).—Apparatus is described. J. S. A.

Refinement of micro-carbon-hydrogen determination by improved weighing technique. A. FRIEDRICH and H. STERNBERG (Mikrochem., Molisch Festschr., 1936, 118—124).—An improved form of absorption tube is described. J. S. A.

Qualitative tests for nitrogen in organic substances. J. B. ROBERTSON (J. S. African Chem. Inst. 1937, 20, 17—20).—The addition of Fe filings (equal in bulk to the substance) to the Na fusion increases the amount of [Fe(CN)₆]⁴⁻ formed, and improves the sensitivity of the test. J. S. A.

Detection of elements in organic compounds. R. H. BAKER and C. BARKENBUS (Ind. Eng. Chem. [Anal.], 1937, 9, 135—136).—A fusion mixture of anhyd. K₂CO₃ and Mg powder (2 : 1) is substituted for Na in the ordinary test for elements. The sample is distilled over the strongly heated fusion mixture in an atm. of Et₂O. J. L. D.

Organic oxidation equivalent analysis. I. Theory and applications. R. J. WILLIAMS. II. Use of iodate (micro and "sub-micro" methods). R. J. WILLIAMS, E. ROHRMAN, and B. E. CHRISTENSEN. III. General method using

dichromate. B. E. CHRISTENSEN, R. J. WILLIAMS, and A. E. KING (J. Amer. Chem. Soc., 1937, 59, 288—290, 291—293, 293—296).—I. The mol. formula of a compound can be calc. from its mol. wt. [suitably corr. if N and/or S (both in reduced condition) are present] and the amount of O necessary for its complete oxidation; equations for compounds containing C, H, and O are given. Possible applications are discussed.

II. The amount of O necessary for complete oxidation can often be determined by treatment with KIO₃ in conc. H₂SO₄ at 185° and back-titration of unused KIO₃; micro (3—4 mg.) and "sub-micro" (0.4—0.6 mg.) methods are detailed (cf. Strebing, A., 1919, ii, 350; Stanek and Nemes, A., 1932, 529). Phthalates are oxidised with difficulty, whilst nicotinic acid is almost unaffected. Oxidation of N is largely avoided under the conditions used.

III (cf. Snethlage, A., 1935, 1140, 1390). The substance (0.05—0.15 g.) is oxidised with K₂Cr₂O₇ in conc. H₂SO₄-H₂O (5 : 1 vol.) at 165—200°, the mixture is then diluted with 6N-H₂SO₄ and boiled gently for 5 min. [to decompose any HCrO₅ or Cr₂(SO₄)₃], and the excess of K₂Cr₂O₇ is determined iodometrically; correction for evolved O₂ is necessary. In some cases (e.g., carbohydrates) CO is produced; this is oxidised with the evolved O₂ over a Pt spiral. The apparatus used is described and the advantages of the method (compared with combustion) are indicated. H. B.

Apparatus for micro-hydrogenation by a volumetric method.—See A., I, 267.

Apparatus for determination of the hydrogenation index. A. CASTILLE (Bull. Soc. chim. Belg., 1937, 46, 5—9).—An apparatus for the accurate determination of the hydrogenation index (100 × wt.-% of H₂ absorbed by the unsaturated compound), by measurement of the H₂ absorbed by approx. 1 g. of the substance in presence of Pt, is described. J. W. B.

Sensitivity of colour reactions for phenols. V. M. PLATKOVSKAJA and S. G. VATRINA (J. Appl. Chem. Russ., 1937, 10, 202—207).—Min. concns. of substance giving a detectable blue colour with phosphomolybdic acid and aq. NH₃ are : PhOH, *o*- and *m*-C₆H₄(OH)₂, 1 : 2 : 3- (I), 1 : 2 : 4- (II), and 1 : 2 : 5-C₆H₃(OH)₃ (III), α -C₁₀H₇·OH, and isoeugenol 0.0005; cresol and quinal 0.00005; β -C₁₀H₇·OH, thymol, and adrenaline 0.005; guaiacolic carbonate 0.05; vanillin 0.1; salicylic acid 0.5%. The vals. with phosphotungstic acid and aq. NH₃ are : *o*- and *p*-C₆H₄(OH)₂ and (I) 0.0005; *m*-C₆H₄(OH)₂ and (II) 0.005; PhOH 0.5%, and with Millon's reagent : PhOH and cresol 0.0005; *o*-C₆H₄(OH)₂ 0.05; (I) 0.5; (III) 5%. R. T.

Turbidity in determination of uric acid with the photo-electric colorimetric.—See A., III, 192.

Sodium cupricyanate. Reaction for cyanuric acid.—See A., I, 256.

Colour reactions of rare earths with alkaloids. III.—See A., I, 263.

Determination of magnesium.—See A., I, 199.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1937.

Method of representing [electromagnetic moments and mesomerism in] organic compounds. A. CORNILLON (Compt. rend., 1937, 204, 694—697).—A scheme for diagrammatic representation of electromagnetic dipoles and mesomeric structures in simple org. compounds. E. W. W.

Formation of graphite in the pyrolysis of organic compounds.—See A., I, 321.

Reactions between atomic deuterium and saturated aliphatic hydrocarbons.—See A., I, 313.

Mercury-sensitised reactions of methane, deuteromethane, and the hydrogen isotopes.—See A., I, 317.

Analysis of saturated and unsaturated gaseous hydrocarbons at very low pressure. R. DELAPLACE (Compt. rend., 1937, 204, 768—770).—A method of separating mixtures of C_2H_6 , C_3H_8 , n - and iso - C_4H_{10} , C_2H_4 , C_3H_6 , Δ^2 - and iso - C_4H_8 , and C_2H_2 , using low-pressure fractionation followed by chemical separation, is discussed. A. J. E. W.

Photo-iodination of the butenes, propylene, and ethylene at low temperatures. Preparation and photolysis of $\alpha\beta$ -di-iodobutane.—See A., I, 318.

Influence of admixtures on polymerisation of butadiene in presence of sodium.—See A., I, 315.

"True" and "conjunct" catalytic polymerisation of olefines. V. N. IPATIEV (Trans. Electrochem. Soc., 1937, 71, Preprint 27, 313—321).—The author's work on the effect of temp., pressure, and concn. on the polymerisation of olefines chiefly by H_3PO_4 and H_2SO_4 is discussed with reference to the formation of (1) polymerides of the reactant ("true polymerisation") and (2) mixtures of products of different types ("conjunct polymerisation"). J. G. A. G.

"Hydro-polymerisation." V. N. IPATIEV and V. I. KOMAREVSKI (J. Amer. Chem. Soc., 1937, 59, 720—722).—Hydrogenation of CMe_2CHMe or iso -butene at 300°/80 kg. per sq. cm. in presence of Fe-NiO and metallic salts ($MgCl_2$, $AlCl_3$, $ZnCl_2$) or H_3PO_4 gives an isodecane, probably $CMe_2EtCHMePr^a$, or isooctane, $CH_2Pr^aBu^a$, respectively. In absence of the salt or H_3PO_4 normal hydrogenation occurs. In absence of Fe-NiO neither hydrogenation nor polymerisation occurs. This simultaneous occurrence of both reactions is termed "hydro-polymerisation." R. S. C.

Fission and isomerisation of olefines. III. Fission of *as*-di*tert*-alkylethylenes and isomerisation of *tert*-alkylvinyl radicals of the general type $CR_3\dot{C}CH_2$. IV. Fission of *as*-*tert*-alkyl-*sec*-alkylethylenes and isomerisation of *sec*-alkylvinyl radicals of the general type, $CHR_2\dot{C}CH_2$. I. N. NASAROV (Ber., 1937, 70, [B], 606—617; 617—624; cf. A., 1936, 819).—III. The ethylenic hydrocarbons when distilled with 1:4- $C_{10}H_6Br\cdot SO_3H$ undergo fission at the point of union with the *tert*-alkyl, giving ultimately a mixture of simpler olefines which are also formed by scission of the methyl*di**tert*-alkylcarbinols. The primary process, $CR_3\dot{C}(CH_2)CR_3 \rightarrow \dot{C}R_3 + CR_3\dot{C}CH_2$, is followed by stabilisation by respective loss and gain of H; union $2\dot{C}R_3 \rightarrow CR_3\cdot CR_3$ is not observed. If the olefine mol. contains two different *tert*-alkyls fission occurs in both possible directions, the order of ease of fission being $Bu^a > CMe_2Pr^a$, $CMe_2Et > CMeEt_2 > CMe_2$, CMe_2Pr^a . CR_3 becomes stabilised to a di- or tri-substituted ethylene by loss of H. The radical $CR_3\dot{C}CH_2$ passes before hydrogenation from the vinyl to the allyl form, so that the ultimate products are mainly tetra-substituted ethylenes. The isomerisation of allyl radicals is fully discussed, and the conclusion is reached that the double linking tends to migrate to the most highly alkylated C. The requisite carbinols are dehydrated by slow distillation in presence of a trace of I. $\gamma\gamma\delta\epsilon\epsilon$ -Pentamethylheptan- δ -ol yields $\gamma\gamma\zeta\zeta$ -tetramethyl- ϵ -methyleneoctane, b.p. 200—204°, transformed into $CMe_2\dot{C}HMe$, (?) $\beta\gamma$ -dimethyl- Δ^2 -pentene (I), and $CMe_2\dot{C}MeEt$. $\delta\delta\epsilon\zeta\zeta$ -Pentamethylnonan- ϵ -ol gives $\delta\delta\eta\eta$ -tetramethyl- ζ -methylenedecane, b.p. 229—233°, whence $CMe_2\dot{C}HET$ (*dimethylpropylcarbinyl chloride*, b.p. 110—113°) and $CMe_2\dot{C}MePr^a$ (oxidised to $COMe_2$, $COMePr$, and a liquid, C_8H_{16} , b.p. 100—105°/22 mm.). $\beta\beta\gamma\delta\delta$ -Pentamethylhexan- γ -ol affords $\beta\beta\delta\delta$ -tetramethyl- γ -methylenehexane, b.p. 176—181°, transformed into $CMe_2\dot{C}HMe$, $CMe_2\dot{C}Me_2$, (I), and $CMe_2\dot{C}MeEt$, which are also derived from $\beta\beta\gamma\delta\delta$ -pentamethylhexan- γ -ol. $\beta\beta\gamma\delta$ -Tetramethyl- δ -ethylhexan- γ -ol gives $\beta\beta\delta$ -tri-methyl- γ -methylene- δ -ethylhexane, b.p. 198—203°, whence C_4H_8 , $CMeEt\dot{C}HMe$, $CMe_2\dot{C}Me_2$, and $CMe_2\dot{C}ET_2$. Dehydration of $\beta\beta\gamma$ -trimethyl- $\delta\delta$ -diethylhexan- γ -ol gives iso - C_5H_{10} , (?) $CMe_2\dot{C}Me_2$, and $CMeEt\dot{C}HET$, and a fraction, C_9H_{18} , b.p. 130—140°. $\beta\beta\gamma\delta\delta$ -Pentamethylheptan- γ -ol affords $\beta\beta\delta\delta$ -tetramethyl- γ -methyleneheptane, b.p. 195—199°, whence iso - C_4H_8 , $CMe_2\dot{C}HET$, $CMe_2\dot{C}Me_2$, and $CMe_2\dot{C}MePr$. $\beta\beta\gamma\delta\delta\epsilon$ -Hexamethylhexan- γ -ol yields $\beta\beta\delta\delta\epsilon$ -pentamethyl- γ -methylenehexane, b.p. 195—200°, whence $CMe_2\dot{C}Me_2$, octene, and $CMe_2\dot{C}MePr^a$.

IV. Olefines $\text{CR}_3\cdot\text{C}(\text{CH}_3)\cdot\text{CHR}_2$ undergo fission to CR_3 which becomes stabilised by loss of H and $\text{CHR}_2\cdot\dot{\text{C}}\cdot\text{CH}_2$ which becomes isomerised to $\cdot\text{CR}_2\cdot\text{CH}\cdot\text{CH}_2$ and thence to $\text{CR}_2\cdot\text{CH}\cdot\text{CH}_2\cdot$, and then stabilised by addition of H, so that the final products are exclusively trisubstituted ethylenes. The isomerisation is entirely one-sided. The second step takes place according to the rule that the double linking tends to become displaced in the direction of the most highly alkylated atom. Dehydration of methylsec.-alkyl-tert.-alkylcarbinols is readily effected by distillation with a trace of I, reaction commencing at about 110—120°. $\beta\gamma\delta\delta$ -Tetramethylhexan- γ -ol gives $\gamma\gamma\epsilon$ -trimethyl- δ -methylenehexane, b.p. 152—156°, whence $\text{iso-C}_4\text{H}_8$, $\text{CMe}_2\cdot\text{CHMe}$, and $\text{CMe}_2\cdot\text{CHEt}$. $\beta\beta\gamma\delta$ -Tetramethylhexan- γ -ol affords $\beta\beta\gamma$ -trimethyl- γ -methylenehexane, b.p. 146—150°, which gives $\text{iso-C}_4\text{H}_8$, $\text{CMe}_2\cdot\text{CHMe}$, and $\text{CMe}_2\cdot\text{CHEt}$. $\beta\delta\delta$ -Trimethyl- γ -methyleneheptane, b.p. 171—174°, from $\beta\gamma\delta\delta$ -tetramethylheptan- γ -ol, yields $\text{CMe}_2\cdot\text{CHMe}$, $\text{CMe}_2\cdot\text{CHEt}$, and $\text{CMePr}^a\cdot\text{CHMe}$. $\beta\beta\gamma\delta$ -Tetramethylheptan- γ -ol affords $\beta\beta\delta$ -trimethyl- γ -methyleneheptane, b.p. 169—174°, whence $\text{iso-C}_4\text{H}_8$, $\text{CMe}_2\cdot\text{CHMe}$, $\text{CMe}_2\cdot\text{CHEt}$, and $\text{CMePr}^a\cdot\text{CHMe}$. Dehydration of $\beta\beta\gamma$ -trimethyl- δ -ethylhexan- γ -ol gives $\beta\beta$ -dimethyl- γ -methylene- δ -ethylhexane, b.p. 169—172°, whence $\text{iso-C}_4\text{H}_8$, $\text{CMe}_2\cdot\text{CHMe}$, $\text{CMe}_2\cdot\text{CHEt}$, and $\text{CMe}_2\cdot\text{CHMe}$. $\beta\beta\gamma\delta\epsilon$ -Pentamethylhexan- γ -ol gives $\beta\beta\delta\epsilon$ -tetramethyl- γ -methylenehexane, b.p. 167—171°, whence $\text{iso-C}_4\text{H}_8$, $\text{CMe}_2\cdot\text{CHMe}$, $\text{CMe}_2\cdot\text{CMe}_2$, and $\text{CHMe}\cdot\text{CMePr}^a$. $\gamma\epsilon$ -Dimethyl- δ -methylene- γ -ethylheptane, b.p. 196—199°, from $\gamma\delta\epsilon$ -trimethyl- ϵ -ethylheptan- δ -ol, gives $\text{CMe}_2\cdot\text{CHMe}$, $\text{CMeEt}\cdot\text{CHMe}$, and $\text{CMeEt}\cdot\text{CHEt}$. $\beta\beta\gamma$ -Trimethyl- δ -propylheptan- γ -ol affords $\beta\beta$ -dimethyl- γ -methylene- δ -n-propylheptane, b.p. 205—207°, whence $\text{iso-C}_4\text{H}_8$ and $\text{CHMe}\cdot\text{CPr}^a_2$. For prep. of the above alcohols see this vol., 225.

H. W.

Hydrogenation of acetylenic compounds. XXVII. Catalytic hydrogenation of $\beta\epsilon$ -dimethyl- Δ^a -hexadien- Δ^2 -ine. J. S. SALKIND and Z. V. SMAGINA (J. Gen. Chem. Russ., 1937, 7, 470—475).— $(\text{C}\cdot\text{CMe}\cdot\text{CH}_2)_2$ and H_2 (Pd catalyst) yield $\beta\epsilon$ -dimethyl- Δ^a -hexene, b.p. 111—113°, which is further hydrogenated to Bu^a_2 in presence of Pt catalyst.

R. T.

Rate of hydration of acetylene.—See A., I, 313.

Technique of introducing radioactive halogens into organic molecules. N. E. BRESHNEVA, S. Z. ROGINSKI, and A. I. SCHILINSKI (J. Phys. Chem. Russ., 1936, 8, 849—865).— EtBr was irradiated by neutrons, and the radioactive Br used for preparing radioactive AlBr_3 . The latter rapidly and completely reacts with EtBr , $\text{C}_5\text{H}_{11}\text{Br}$, $(\text{CH}_2\text{Br})_2$, CH_2PhBr , etc.; the exchange with PhBr , $p\text{-C}_6\text{H}_4\text{Br}_2$, and $1\text{-C}_{10}\text{H}_7\text{Br}$ is slow. AlBr_3 reacts also with CHCl_3 and CCl_4 but not with EtI . Radioactive AlCl_3 does not exchange with bromides and iodides; AlI_3 reacts with both chlorides and bromides.

J. J. B.

Photochemical formation of tetrachloroethane from trans-dichloroethylene and chlorine.—See A., I, 318.

Addition of hydrogen bromide to allyl bromide

in the presence of various substances. V. Comparison of the effect of oxygen with that of peroxide. Relation between the amount of oxygen present and the result of addition. Y. URUSHIBARA and M. TAKEYASHI (Bull. Chem. Soc. Japan, 1937, 12, 138—144).—Previous results (this vol., 81) are confirmed and O_2 is shown to possess catalytic activity in the sense of, and $>$, the "peroxide effect." The activity is influenced by impurities in the allyl bromide. F. R. G.

Anomalous elimination of halogens from certain tri- and tetra-halides. A. A. PETROV and A. F. SAPOSHNIKOVA (J. Gen. Chem. Russ., 1937, 7, 476—484).—When heated with KOH in aq. EtOH , compounds, $\text{CHMeX}\cdot\text{CMeX}_2$, yield $(\cdot\text{CMeX})_2$, and of the type $(\text{CMeX}_2)_2$ yield $(\text{CH}_2\cdot\text{CX})_2$. Thus $\text{CHMeBr}\cdot\text{CMeBr}_2$ gives $(\cdot\text{CMeBr})_2$ (I), and $(\cdot\text{CMeBr}_2)_2$ gives $\text{CH}_2\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CH}_2$. $\text{CHMe}\cdot\text{CMeCl}$ (II) and Br yield β -chloro- $\gamma\gamma$ -dibromobutane, b.p. 66—66.5°/12 mm., which reacts with KOH to yield $\text{CMeCl}\cdot\text{CMeBr}$ (III), from which β -chloro- $\beta\gamma\gamma$ -tribromobutane, m.p. 223—224°, is obtained, and this regenerates (III) when treated with EtOH-KOH . (II) and ClI in HCl afford $\beta\beta$ -dichloro- γ -iodobutane, b.p. 69.5°/11.5 mm., from which (II) is regenerated by heating with EtOH-KOH . $\text{CHMe}\cdot\text{CMeBr}$ (IV) and ClI give a mixture of β -chloro- β - and γ -bromo- γ -iodobutane, yielding (II) and (III) with EtOH-KOH . (IV) and BrI yield a mixture of $\beta\beta$ - and $\beta\gamma$ -dibromo- γ -iodobutane, giving (I) and (IV) with EtOH-KOH .

R. T.

Synthesis of derivatives from $\alpha\gamma$ -dichloro- Δ^a -butene. Use of by-products from synthesis of chloroprene. A. L. KLEBANSKI and K. K. TSCHERVUICHALOVA (Sintet. Kautschuk, 1935, No. 6, 16—21).— $\alpha\gamma$ -Dichloro- Δ^a -butene (I) with EtOH-KOH affords γ -chloro- α -ethoxy- Δ^a -butene, b.p. 62—64°/40 mm., whereas aq. Na_2CO_3 affords γ -chloro- Δ^a -buten- α -ol (II), b.p. 92°/50 mm. (xanthate). (I) and (II), with aq. KOH , yield di-(γ -chloro- Δ^a -butenyl) ether, b.p. 142°/50 mm. (I) yields chloroprene when passed over various catalysts at high temp. CH. Abs. (r)

Formation of chloronitroso-compounds from ethylenic hydrocarbons (C_6 to C_{11}). M. TUOT (Compt. rend., 1937, 204, 697—699).—Hydrocarbons of type $\text{CRR}'\cdot\text{CHR}''$ or $\text{CRR}'\cdot\text{CR}''\text{R}'''$ react readily, those of type $\text{CHR}\cdot\text{CHR}'$ with difficulty, with NOCl (from $\text{C}_5\text{H}_{11}\cdot\text{O}\cdot\text{NO}$, or, better, from $\text{SOCl}_2 + \text{N}_2\text{O}_3$ mixed with the hydrocarbon at -5°) to form chloronitrosoparaffins (or chloro-oximes). The following compounds are prepared: from $\text{CHMe}\cdot\text{CMeEt}$, $\text{C}_6\text{H}_{12}\text{ONCl}$, m.p. 66°; from $\text{CMe}_2\cdot\text{CHPr}^a$, $\text{C}_7\text{H}_{14}\text{ONCl}$, m.p. 67°; from $\text{CHMe}\cdot\text{CEt}_2$, $\text{C}_7\text{H}_{14}\text{ONCl}$, m.p. 86°; from $\text{CMe}_2\cdot\text{CHBu}^a$, $\text{C}_8\text{H}_{16}\text{ONCl}$, m.p. 123°; from $\text{CMeEt}\cdot\text{CHBu}^a$, $\text{C}_9\text{H}_{18}\text{ONCl}$, m.p. 113°; from $\text{CMe}_2\cdot\text{CMeBu}^a$, $\text{C}_9\text{H}_{18}\text{ONCl}$, m.p. 158°; and from $\text{CMeBu}^a\cdot\text{CHBu}^a$, $\text{C}_{11}\text{H}_{22}\text{ONCl}$, m.p. 109°.

E. W. W.

Nitration of paraffins by nitrogen peroxide. T. URBANSKI and M. SLON (Compt. rend., 1937, 204, 870—871; cf. A., 1936, 1485).— $n\text{-C}_5\text{H}_{12}$ with N_2O_4 at 200° affords mono-, b.p. 164—165°/750.3 mm. (60%), and di-nitropentane (40%). $n\text{-C}_6\text{H}_{14}$ and $n\text{-C}_7\text{H}_{16}$ similarly give $(\text{NO}_2)_1$, b.p. 185°/780.3 mm.

and b.p. 199—200°/750.3 mm., and $(NO_2)_2$ -derivatives, respectively. $n\text{-C}_3\text{H}_{18}$ and $n\text{-C}_9\text{H}_{20}$ afford mixtures which decompose when distilled. J. L. D.

Aliphatic nitro-compounds. IV. Reactions of nitromethane halides with metal-organic compounds. N. N. MELNIKOV (J. Gen. Chem. Russ., 1937, 7, 456—460).—The following reactions are described: $CX_3\cdot NO_2$ (I) + $4MgPhX \rightarrow OR\cdot MgX + Ph_2 + MgO, MgX + CX_3\cdot NPh\cdot MgX$; (I) + $3HgEt_2 \rightarrow CEt_3\cdot NO_2 + 3HgEtX$ (II); $3C_4H_{10} + 6(II) + N_2 + 2CO_2 \leftarrow 2(I) + 6HgEt_2 \rightarrow 3C_4H_{10} + 6(II) + 2CO + 2NO$; $Ph_3X_2 + N_2 + 2CO_2 \leftarrow 2(I) + 3PPh_3 \rightarrow 3PPh_3X_2 + 2NO + 2CO$ (X = Cl, Br). R. T.

Biochemical hydrogenations. IV. Hydrogenation of crotyl alcohol by coli bacteria. F. G. FISCHER and W. ROBERTSON (Annalen, 1937, 529, 84—87; cf. A., 1936, 588).—Crotyl alcohol in concn. 1:1000 does not appreciably restrict the growth of the bacteria or fermentation; its partial reduction is established. Indecisive results are obtained with $CHPh\cdot CH\cdot CH_2\cdot OH$. H. W.

Synthesis of tertiary alcohols $CR_3\cdot CMe(OH)\cdot CHR_2$ and $CR_3\cdot CMe(OH)\cdot CR_3$. Action of magnesium methyl bromide on branched ketones. I. N. NASAROV (Ber., 1937, 70, [B], 599—605).—Ketones $CR_3\cdot CO\cdot CHR_2$ and $CO(CR_3)_2$ are converted by $MgMeBr$ into the corresponding *tert.*-alcohols without formation of by-products. The difficulty of the action increases when Me (= R) is replaced by Et and particularly by Pr^i , but is not greatly altered when Pr^i replaces Me; it also increases on passage from $CR_3\cdot CO\cdot CHR_2$ to $CO(CR_3)_2$. Very little *tert.*-alcohol results from the ketone and $MgEtBr$ or $MgPr^iBr$, the main change being reduction to the *sec.*-alcohol. Methylethylpinacolin and $MgMeBr$ afford $\beta\gamma\delta$ -tetramethylhexan- γ -ol, b.p. 190—193°. The following alcohols are obtained analogously: $\beta\gamma\delta\delta$ -tetramethylhexan- γ -ol, b.p. 197—199°; $\beta\beta\gamma$ -trimethyl- δ -ethylhexan- γ -ol, b.p. 208—211°; $\gamma\delta\epsilon$ -trimethyl- γ -ethylheptan- δ -ol, b.p. 235—238°; $\beta\beta\gamma$ -trimethyl- δ -propylheptan- γ -ol, b.p. 234—237.5°; $\beta\beta\gamma\delta$ -tetramethylheptan- γ -ol, b.p. 212—215°; $\beta\gamma\delta\delta$ -tetramethylheptan- γ -ol, b.p. 215—217°; $\beta\beta\gamma\delta\epsilon$ -pentamethylhexan- γ -ol, b.p. 207—210°; $\beta\beta\gamma\delta\delta$ -pentamethylhexan- γ -ol, b.p. 219—222°; $\beta\beta\gamma\delta$ -tetramethyl- δ -ethylhexan- γ -ol, b.p. 237—240°; $\gamma\gamma\delta\epsilon\epsilon$ -pentamethylheptan- γ -ol, b.p. 243—246°; $\beta\beta\gamma$ -trimethyl- $\delta\delta$ -diethylhexan- γ -ol, b.p. 252—256°; $\delta\delta\epsilon\zeta\zeta$ -pentamethylnonan- ϵ -ol, b.p. 266—269°; $\beta\beta\gamma\delta\delta$ -pentamethylheptan- γ -ol, b.p. 233—235°; $\beta\beta\gamma\delta\delta\epsilon$ -hexamethylhexan- γ -ol, b.p. 235—238°. H. W.

Sulphuric [acid] dehydration of divinyl glycol. Hydrobenzoin type of rearrangement with migration of the vinyl group. M. TIFFENEAU and P. WEILL (Compt. rend., 1937, 204, 590—592).— $[CH_2\cdot CH\cdot CH(OH)]_2$ with 50% H_2SO_4 at 100—120° gives a 40—50% yield of a mixture, b.p. 140—150°, containing mainly α -vinylcrotonaldehyde, reduced (Raney Ni) with H_2 to give α -ethylcrotonaldehyde (semicarbazone, m.p. 210°) (synthesised from Pr^iCHO and $MeCHO$ and dehydration of the aldol), and with $3H_2$ to give $CH_3CH_2\cdot CH_2\cdot OH$.

No trace of Δ^1 -cyclopentene-1-aldehyde (Urien, A., 1934, 389) was detected. J. W. B.

Catalytic and acid dehydration of divinyl glycol. E. URIEN and E. BAUM (Compt. rend., 1937, 204, 595—597).— α -Vinylcrotonaldehyde (I) (preceding abstract) is not converted into Δ^1 -cyclopentene-1-aldehyde (II) by passage over Al_2O_3 at 320°. (I) is also obtained in very small yield from divinyl glycol (III) and boiling 2% H_2SO_4 . Temp. is the main factor which determines the formation of (I) (<200°) or (II) (>200°) by dehydration of (III). Thus (III) and 8% H_2SO_4 at 200—210° give some (II). No dehydration of (III) could be effected with Al_2O_3 at <200°/7—8 mm. J. W. B.

Action of formic acid on tetraethylbutinediol. V. N. KRESTINSKI and N. I. SUMM (J. Gen. Chem. Russ., 1937, 7, 440—455).— $(C\cdot CEt_2\cdot OH)_2$ and HCO_2H or 20% H_2SO_4 at 80° yield γ -diethyl- Δ^8 -octadien- Δ^8 -ine, b.p. 169—171°, which yields $AcOH$, $EtCO_2H$, $OH\cdot CHMe\cdot CEt(OH)\cdot CO_2H$, and $OH\cdot CEtAc\cdot CO_2H$ with $KMnO_4$, γ -diethyl- Δ^8 -octene (I), b.p. 198° (dibromide, b.p. 114—115°/4 mm.), with H_2 in presence of Pd, and γ -diethyloctane in presence of Pt catalyst. (I) is oxidised by $KMnO_4$ to $AcOH$, $EtCO_2H$, and $CH_3CH_2\cdot CO_2H$. R. T.

Derivatives of the oxidation products of glycerol. H. P. DEN OTTER (Rec. trav. chim., 1937, 56, 474—491).—Glycerol oxidised with H_2O_2 and $FeSO_4$ yields glyceraldehyde, $OH\cdot CH_2\cdot CO\cdot CHO$ (I), HCO_2H , and $AcCHO$; with $NaOCl$ or $Ca(OCl)_2$, CH_2O and (probably) β -acrose are formed, whilst with Br and Na_2CO_3 , dihydroxyacetone (II) is obtained. From glyoxal, the following are prepared: 3-nitro-, m.p. 292°, 5-chloro-2-nitro-, m.p. 319—320°, 5-bromo-2-nitro-, m.p. 320—325° (decomp.), and 4:6-dinitro-3-ethoxyphenyl-, m.p. 330° (decomp.), o-, m.p. 105—106°, m-, m.p. 125—126°, p-tolyl-, m.p. 224° (decomp.), α -, m.p. 211°, and β -naphthyl-osazone, m.p. 252°. Dihydroxyacetone-5-chloro-2-nitro-, m.p. 136°, 5-bromo-2-nitro-, m.p. 155—156°, and 4:6-dinitro-3-ethoxyphenylhydrazones, m.p. 124—126°, and -2-nitro-, m.p. 210°, -3-nitro-, m.p. 192°, -5-chloro-2-nitro-, m.p. 244°, -5-bromo-2-nitro-, m.p. 256—258° (decomp.), -4:6-dinitro-3-ethoxyphenyl-, m.p. 296°, and -benzoyl-osazone, m.p. 220°, are described. Oxidation $[Cu(OAc)_2]$ of (II) affords (I) which yields the following derivatives which cannot be formed from (II) and the appropriate hydrazine: dihydroxyacetone-phenylmethyl-, m.p. 145°, -o-, m.p. 145—148°, -m-, m.p. 156°, and -p-tolyl-, m.p. 167°, -diphenyl-, m.p. 241°, and -phenylbenzyl-osazone, m.p. 194°. The phenyl-osazone of (II) with $PhCHO$, HCl , or glucose does not yield (I). J. D. R.

Preparation of synthetic ethers from α -chloroethers. H. I. WATERMAN, W. J. C. DE KOK, J. J. LEENDERTSE, and W. H. SCHOENMAKER (Rec. trav. chim., 1937, 56, 437—441).—The reaction $CH_2R\cdot OR' + MgR''\cdot X \rightarrow CHRR''\cdot OR'$ has been applied to the synthesis of $OEt\cdot CHMeEt$, $OEt\cdot CHMe\cdot C_5H_{11}\cdot n$, and $CH_2Ph\cdot O\cdot CH_2Bu^i$. Physical consts. are recorded. J. D. R.

Chlorination of propylene oxide. A. F. DOBRIANSKI, M. I. DAVIDOVA, and Z. T. PANKINA (J.

Gen. Chem. Russ., 1937, 7, 291—297).—The chief product of chlorination at 0° is $\text{COMe}\cdot\text{CH}_2\text{Cl}$, together with other compounds, of which $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl}$ is identified. R. T.

Preparation of divinyl ether. W. A. LOTT, F. A. SMITH, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1937, 26, 203—208).—The ether is obtained in yields of 21—36% from $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$ with solutions of KOH or, e.g., Na *tert.*-hexoxide in higher alcohols (e.g., octyl). F. O. H.

Syntheses of glycerides with the aid of triphenylmethyl compounds. III. Triglycerides. P. E. VERKADE, J. VAN DER LEE, and (ERL.) W. MEERBURG (Rec. trav. chim., 1937, 56, 365—374).— γ -Triphenylmethylglyceryl α -stearate (A., 1936, 704) with myristyl chloride (I) in dry quinoline- CHCl_3 at room temp. affords γ -triphenylmethylglyceryl β -myristate α -stearate, m.p. 43.5—44°, which with HCl (gas) in cold Et_2O affords *glyceryl* γ -myristate α -stearate, m.p. 66—66.5°. γ -Triphenylmethylglyceryl α -palmitate likewise affords γ -triphenylmethylglyceryl β -myristate α -palmitate, m.p. 27—28°, whence *glyceryl* γ -myristate α -palmitate (II), m.p. 63.5—64°. *Glyceryl* γ -palmitate α -stearate similarly affords *glyceryl* β -myristate γ -palmitate α -stearate, m.p. 59.5—60° (labile form, m.p. 55—56°). Similarly, *glyceryl* γ -myristate α -stearate gives *glyceryl* γ -myristate β -palmitate α -stearate, m.p. 58.5—59°, and (II) gives *glyceryl* γ -myristate α -palmitate β -stearate, m.p. 58.5—59°. J. L. D.

Thioglycerols. H. RHEINBOLDT and C. TETSCH (Ber., 1937, 70, [B], 675—680).—Gradual addition of $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ to a solution of NaHS in abs. EtOH at 65° gives β -hydroxy- $\alpha\gamma$ -dithiolpropane ($\alpha\gamma$ -dithioglycerol), b.p. 94°/12 mm. (Hg, m.p. 185°, and Pb, decomp. 175—180° after darkening at 130°, compounds). Analogously $\text{CHBr}(\text{CH}_2\text{Br})_2$ affords $\alpha\beta\gamma$ -trithiolpropane (trithioglycerol), b.p. 115—120°/12 mm., insol. in H_2O , sol. in Et_2O ; it gives a Hg compound, $\text{C}_6\text{H}_{10}\text{S}_6\text{Hg}_3$, decomp. about 170°, Pb derivative, incipient decomp. 130°, Ag compound, gradual decomp. >150°; it is transformed by Me_2SO_4 and NaOH into $\alpha\beta\gamma$ -trimethylthiolpropane, b.p. 147°/15 mm., oxidised by H_2O_2 in AcOH to the corresponding trisulphone, m.p. 206°. *Trihioglyceryl tripalmitate*, $\text{C}_3\text{H}_5(\text{S}\cdot\text{CO}\cdot\text{C}_{15}\text{H}_{31})_3$, has m.p. 71°. H. W.

Ethyl ethylsulphenate. A. MEUWSEN and H. GEBHARDT (Ber., 1937, 70, [B], 792—796).—Interaction of EtOCl with NaSEt in Et_2O affords Et_2S_2 . SET·SCN and NaOEt in Et_2O yield *Et ethylsulphenate* (I), SET·OEt, b.p. 38.2—38.5°/50 mm., 107.8—108.5°/724 mm., which is not readily autoxidised, does not reduce SeO_2 to Se, and does not give well-defined products with NO_2 or KMnO_4 in COMe_2 . It is smoothly oxidised by EtOCl in Et_2O to *Et ethylsulphinate* (II), b.p. 62—63°/15—16 mm.; analogously $\text{S}(\text{OEt})_2$ affords $\text{SO}(\text{OEt})_2$. Ozonisation of (I) in CCl_4 at about -20° gives (II), whereas at room temp. *Et ethylsulphonate* is produced; Et_2S and Et_2SO are similarly oxidised to Et_2SO_2 . Hydrolysis of (I) by $\text{Ba}(\text{OH})_2$ -MeOH leads to *Ba ethylsulphinate*. Mg ethylsulphinate and HgCl_2 afford the compound $(\text{EtSO}_2)_2\text{Hg}\cdot\text{HgCl}_2$. H. W.

Action of the sulphonyl group. F. ARNDT (J. Amer. Chem. Soc., 1937, 59, 759—760).— SO_3H promotes enolisation by diminishing the prototropic expenditure of work necessary; CO_2H promotes it directly by increasing the electromeric effect of the mol. The difference in degree of enolisation caused by these groups is thus due to a difference in the nature of the mechanism (cf. Kohler *et al.*, this vol., 23). R. S. C.

Reaction between sulphur dioxide and olefines. V. Structure of the polysulphones from olefines of the type $\text{CHR}\cdot\text{CH}_2$. F. J. GLAVIS, L. L. RYDEN, and C. S. MARVEL (J. Amer. Chem. Soc., 1937, 59, 707—711; cf. A., 1936, 1487).—By further examples (cf. A., 1935, 1349) it is shown that olefines, $\text{CHR}\cdot\text{CH}_2$, condense with SO_2 to head-head-tail-tail polymeric sulphones (A), $\dots \text{CH}_2\cdot\text{CHR}\cdot\text{SO}_2\cdot[\text{CHR}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CHR}\cdot\text{SO}_2]_x\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\dots$. Δ^a -Pentenepolysulphone (A; R = Pr^a) with hot 20% NaOH gives Pr^aCHO and Na α -methylsulphonyl-*n*-pentane- β -sulphinat, + H_2O , oxidised by H_2O_2 to the corresponding sulphonate (I), which gives the sulphonyl chloride (II), m.p. 64—65°. Δ^a -Pentene and HOCl give α -chloropentane- β -ol, b.p. 68—75°/30 mm., and thence successively α -methylthiolpentane- β -ol (by NaSMe), b.p. 90°/18 mm., β -chloro- α -methylthiolpentane (by SOCl_2), b.p. 84—86°/20 mm., Na α -methylthiolpentane- β -sulphonate (by $\text{Na}_2\text{S}_2\text{O}_3$), (I) (by KMnO_4), and (II). The polysulphones from C_3H_6 , Δ^a - C_3H_{10} , C_3H_{16} , C_3H_{18} , and styrenepolysulphone (A; R = Ph), m.p. 185—190°, give 2:6-disubstituted 1:4-dithian 1:4-bisdioxides, $\text{SO}_2\langle\text{CHR}\cdot\text{CH}_2\rangle\text{SO}_2$, in which R = Me, m.p. 334°, Pr^a, m.p. 257°, *n*- C_8H_{14} , m.p. 265°, *n*- C_7H_{16} , m.p. 260—261°, and Ph, m.p. 280°. The original olefine (C_3H_6 , etc.), when treated first with S_2Cl_2 [gives probably $\text{S}(\text{CH}_2\cdot\text{CH}_2\text{R})_2$] and then with Na_2S in dry EtOH, gives 2:6-di-methyl-, b.p. 85—87°/12 mm., *n*-propyl-, b.p. 145—155°/20 mm., and *phenyl*-1:4-dithian, b.p. 190—195°/30 mm., oxidised by H_2O_2 to the bisdioxides. R. S. C.

Reactions of mercury diethyl with certain acid chlorides. N. N. MELNIKOV and M. S. ROKITSKAJA (J. Gen. Chem. Russ., 1937, 7, 464—466).— HgEt_2 reacts with R·COCl or OR'·COCl to yield respectively COEtR or $\text{EtCO}_2\text{R}'$, with HgEtCl (R = Me, Bu⁶, Ph; R' = Me, Et). R. T.

Electrolytic dissociation processes. II. Friedel-Crafts reaction.—See A., I, 320.

Oxidation of acetic, propionic, butyric, and isovaleric acids by molecular oxygen with ultra-violet light.—See A., I, 318.

Electrolysis of deuterio-fatty acids. I. Electrolysis of deuterioacetic acid. P. HÖLEMANN and K. CLUSIUS (Z. physikal. Chem., 1937, B, 35, 261—269).—The electrolysis of $\text{CD}_3\cdot\text{CO}_2\text{D}$ and $\text{CD}_3\cdot\text{CO}_2\text{Na}$ in H_2O and of AcOH in D_2O has been investigated. Only with the solutions in H_2O does the C_2H_6 given off contain D, which shows that there is no interchange of D and H between the solvent and the Me formed as intermediate product in the production of C_2H_6 . A

micro-balance for determining the d of C_2H_6 is described.

R. C.

Electrolysis of fatty acids containing deuterium. II. Mechanism of the formation of ethylene during the electrolysis of propionic acid. P. HÖLEMANN and K. CLUSIUS (Ber., 1937, 70, [B], 819—827).—Examination of the products obtained by the electrolysis of $CD_3 \cdot CH_2 \cdot CO_2H$ and $CD_3Me \cdot CO_2D$ shows that in the production of C_2H_4 by the electrolysis of $EtCO_2H$ the primary dehydrogenation of Et occurs by loss of H from Me . Et is regarded as a semi-prepared C_2H_4 in which a marked strengthening of the $C-C$ linking has occurred with consequent considerable weakening of the $C-H$ linking. The subsidiary production of C_2H_6 is ascribed to disproportionation of C_2H_4 ; this is justified from the viewpoint of energy. $\beta\beta\beta$ -Trideuteropropionic acid is obtained by the electrolysis of a solution of $CD_3 \cdot CO_2K$ and $CO_2K \cdot CH_2 \cdot CO_2Et$ in H_2O as catholyte and 25% K_2CO_3 as anolyte with Pt electrodes in a U-tube provided with a glass-wool plug; a stream of CO_2 is passed through the catholyte. The ester mixture is separated by distillation under diminished pressure at 0° and the appropriate fraction is hydrolysed. Trideuteroacetic deuteracid is prepared by heating $CHMe(CO_2H)_2$ with 99.21% D_2O at 55° .

H. W.

Influence of cis-trans-isomerism on selective hydrogenation. V. P. GOLENDEEV (J. Gen. Chem. Russ., 1937, 7, 317—327).—The allyl double linkings of allyl oleate (I) or elaidate (II) are hydrogenated (160° ; Pd- $BaSO_4$ catalyst) before those of the acids, and of (II) before those of (I). The velocity of hydrogenation of the acid double linking of (I) $>$ of (II).

R. T.

Transposition of the double linking in Δ^4 - and Δ^6 -oleic acid. I. I. VANIN and A. A. TSCHERNJAROVA (Ber., 1937, 70, [B], 624—628).—A fuller account of work already reported (A., 1936, 705).

H. W.

Synthesis of unsaturated fatty acids. II. Linoleic and λ - n -amyl- Δ^8 -tridecadienoic acids. C. R. NOLLER and M. D. GIRVIN (J. Amer. Chem. Soc., 1937, 59, 606—608; cf. A., 1934, 991).— Δ^8 -Octen- β -ol (from $CH_2 \cdot CH \cdot CHO$ and $C_5H_{10} \cdot MgBr$), b.p. $78-81^\circ/20$ mm., and PBr_3 give a mixed bromide, b.p. $87-89^\circ/20$ mm., the Grignard reagent from which with θ -chloro- $\alpha\beta$ -dibromo- α -methoxynonane gives a product, converted by Zn etc. into impure Δ^8 -heptadecadienyl chloride, b.p. $165-171^\circ/6$ mm., which with KCN gives the impure cyanide, b.p. $185-187^\circ/3$ mm., hydrolysed to an oily acid. This acid gives no oleic acid tetrabromide before or after elaidinisation, but yields α - and β -sativic acid and thus contains some oleic acid; the presence of $>30\%$ of κ -vinyl- Δ^6 -hexadecenoic acid is indicated by formation of 0.16 mol. of CH_2O by O_3 (pure undecenoic acid gives only 0.44 mol.).

R. S. C.

Naturally occurring linoleic acid in cottonseed and soya-bean oils and the regenerated linoleic acid from α -linoleic acid tetrabromide of these oils. D. M. BROSEL (J. Amer. Chem. Soc., 1937, 59, 689—692).—The free fatty acids of soya-bean and cottonseed oils with $KMnO_4$ give only α - (I) and

β -sativic acid (II) and with Br only α -linoleic acid tetrabromide (III); the α -linoleic acid regenerated from (III) yields only (III) with Br , and only (I) and (II) with $KMnO_4$.

R. S. C.

Configurative relationship of α -hydroxy- n -valeric and α -hydroxyisovaleric acids. P. D. BARTLETT, M. KUNA, and P. A. LEVENE (J. Biol. Chem., 1937, 118, 503—511).—*iso*Propylcrotylcarbinol, b.p. $51-54^\circ/15$ mm., prepared from $CHMe \cdot CH \cdot CHO$ and $Pr^{\beta}Br$, yields the (+)-carbinol (I), same b.p., $[\alpha]_D^{25} +19.36^\circ$ [H phthalate, $[\alpha]_D^{25} +16.8^\circ$ in $EtOH$ (strychnine salt, sets at -10°)], which is ozonised to (—)- α -hydroxyisovaleraldehyde (II), $[\alpha]_D^{25} -5.4^\circ$ in Et_2O ; this could not be satisfactorily converted into the acid. Reduction ($Na-Hg$) of (II) gives (+)- β -methylbutane- $\gamma\delta$ -diol, b.p. $103^\circ/12$ mm., $[\alpha]_D^{25} +3.9^\circ$ in Et_2O , which could not be catalytically reduced. (I) is hydrogenated (Adams) to (+)-propylisopropylcarbinol (III), b.p. $52^\circ/12$ mm., $[\alpha]_D^{25} +15.03^\circ$. (—)-*iso*Propylcrotylcarbinol (IV), $[\alpha]_D^{25} -11.4^\circ$, yields an *Ac* derivative, b.p. $86-87^\circ/46$ mm., $[\alpha]_D^{25} +21.3^\circ$, which with $KMnO_4 \cdot COMe_2$ forms (+)- α -acetoxisovaleric acid (V), b.p. $95-97^\circ/3$ mm., $[\alpha]_D^{25} +8.62^\circ$ (*Me* ester, b.p. $50^\circ/1$ mm., $[\alpha]_D^{25} +9.25^\circ$). (+)- α -Hydroxyisovaleric acid, from *d*-valine or from α -bromoisovaleric acid, has a small + rotation, dependent on concn., which changes to a — rotation in the *Na* salt; the *Et* ester, b.p. $112-114^\circ$, has $[\alpha]_D^{25} +0.30^\circ$ [*Ac* derivative (VI), b.p. $80^\circ/10$ mm., $[\alpha]_D^{27} -9.83^\circ$].

(—)- α -Hydroxy- n -valeric acid (VII) has previously been correlated with (+)- $CHMePr^{\alpha}OH$, and thus with (III) and with (I); from the relationships of (IV), (V), and (VI), it follows that (—)- α -hydroxyisovaleric acid is configuratively related to (VII). E. W. W.

Configurative relationship of α -hydroxy- n -hexoic and α -hydroxyisohexoic acids. P. D. BARTLETT, M. KUNA, and P. A. LEVENE (J. Biol. Chem., 1937, 118, 513—517).—(—)-*iso*Butylcrotylcarbinol (I), $[\alpha]_D -1.46^\circ$ (resolution through the strychnine salt of the *H* phthalate, which when heated gives a substance, b.p. $30^\circ/12$ mm., probably ζ -methyl- Δ^8 -heptadiene), is hydrogenated to (+)-propylisobutylcarbinol (II), b.p. $72^\circ/15$ mm., $\alpha +3.00^\circ$, and is ozonised to (+)- α -hydroxyisohexaldehyde, b.p. $79^\circ/18$ mm., $[\alpha]_D^{25} +6.0^\circ$. In C_5H_5N with Ac_2O , (I) gives its *Ac* derivative, b.p. $88-90^\circ/30$ mm., $[\alpha]_D^{25} +13.7^\circ$, which with $KMnO_4 \cdot COMe_2$ yields (+)- α -acetoxisohexoic acid, b.p. $127^\circ/5$ mm., $[\alpha]_D^{25} +9.91^\circ$ [*Me* ester (III), b.p. $68^\circ/5$ mm., $[\alpha]_D^{27} +10.5^\circ$]. (—)- α -Hydroxyisohexoic acid, $[\alpha]_D^{25} -11.8^\circ$ (from *l*-leucine), is converted into the *Et* ester, b.p. $118^\circ/90$ mm., $[\alpha]_D^{25} -7.06^\circ$ [*Ac* derivative (IV), b.p. 74° , $[\alpha]_D^{27} -34.8^\circ$]. (—)- α -Hydroxy- n -hexoic acid (V) has already been correlated with (+)-methyl- n -butylcarbinol, and thus with (II) and (I); from the above relationships, and the rotations of (III) and (IV), it is seen that (V) is configuratively related to (+)- α -hydroxyisohexoic acid. As (V) and (—)- α -hydroxy- n -valeric acid have the same configuration, α -hydroxyisovaleric and isohexoic acids of the same configuration have opposite rotations; thus the effect of Pr^{β} on the rotation of OH-acids varies with its distance from the asymmetric C-atom. *iso*Butylvinylcarbinol could not be resolved.

E. W. W.

Catalysis of maleic-fumaric acid isomerisation by hydrogen ions. C. HORREX (Trans. Faraday Soc., 1937, 33, 570—571).—Fumaric acid obtained by heating maleic acid with 2*N*-DCl in 99.5% D₂O and recrystallising twice from a large excess of H₂O contains no D. Since, if the isomerisation with acids proceeds by way of the addition of H⁺ or HX at the double linking, the added H atom cannot be the one eliminated, the above observation indicates that the geometrical inversion does not proceed by this mechanism. F. L. U.

Catalytic hydrogenation and esterification of C₁-saccharolactones and the hydrogenation of butyl erythronate. J. W. E. GLATTFELD and (Miss) A. M. STACK (J. Amer. Chem. Soc., 1937, 59, 753—759).—Na βγ-dihydroxybutyrate and AcCl at 50—85° give 57% of β-acetoxy-γ-butyrolactone (I), b.p. 119—121°/4 mm., and 9.6% of (?) *trans*-γ-acetylcrotonic acid, m.p. 99—102°. Hydrogenation of β-hydroxy-γ-butyrolactone (II) at <120 atm. in presence of PtO₂, Cu-Cr, Pd, Cu-Ba-Cr, Cu-Cr (57 atm.), or Raney Ni gives γ-butyrolactone, also obtained from (I) by H₂-PtO₂ at 129 atm., but similar reduction of α-hydroxy-γ-butyrolactone (III), βγ-dihydroxybutyramide, erythronolactone, and erythronamide gives indefinite results. Hydrogenation of (II) and (III) in H₂O occurred at 2—3 atm. (PtO₂), but the products were not isolated. Bu erythronate in 95% EtOH with H₂-PtO₂ at 2—3 or 95 atm. gives good yields of erythritol. Esters of the dihydroxy-acids could not be obtained. (II) with H₂SO₄-BuOH gives Bu β-hydroxyisocrotonate, b.p. 174—181°/2 mm., with EtOH-H₂SO₄-anhyd. CaSO₄ gives γ-crotonolactone, and with HCl-EtOH gives Et γ-chloro-β-hydroxybutyrate, b.p. 92—95°/4 mm. (III) gives similarly Et γ-chloro-α-hydroxybutyrate, b.p. 92—95°/1—5 mm. R. S. C.

Duality of oxidised forms and polarisation of vitamin-C.—See A., III, 232.

Determination of ascorbic acid.—See A., III, 233.

Stabilisation of ascorbic acid by metaphosphoric acid. K. HINSBERG (Biochem. Z., 1937, 290, 125—128).—A solution of ascorbic acid in 50% HPO₃ retains its titre almost unchanged for days whereas when treated with CCl₃·CO₂H it is rapidly destroyed. P. W. C.

Glucoscorbic acid. W. N. HAWORTH, E. L. HIRST, and J. K. N. JONES (J.C.S., 1937, 549—556).—*d*-Glucoscorbic acid (improved prep.) [*phenylosazone* (?), m.p. 215°] with CH₂N₂ in MeOH-Et₂O affords 3-methyl-*d*-glucoscorbic acid, m.p. 142°, [α]_D²⁰ -25° in H₂O, further converted by CH₂N₂ in MeOH into 2:3-dimethyl-*d*-glucoscorbic acid (I), m.p. 94°, [α]_D²⁰ -22° in H₂O, -7° in MeOH, which, after repeated methylation (MeI-Ag₂O) in anhyd. COMe₂, yields trimethylisopropylideneglucoscorbic acid, b.p. 150° (bath)/0.04 mm., [α]_D²¹ -1.6° in MeOH. Hydrolysis of this followed by repeated methylation (MeI-Ag₂O) affords 2:3:5:6:7-pentamethylglucoscorbic acid, m.p. 80°, [α]_D²⁰ -5° in MeOH, +21° in CCl₄, oxidised (O₃ in CCl₄) to 3:4:5-trimethyl-*d*-arabonic acid, m.p. 67°, [α]_D¹⁹ +5° in MeOH {*Me* ester, b.p.

110° (bath)/0.03 mm., [α]_D¹⁸ -17.5° in MeOH; *amide*, m.p. 51°, [α]_D¹⁸ -30° in H₂O, which with MeI-MeOH-Ag₂O affords *Me* 2:3:4:5-tetramethyl-*d*-arabonate, b.p. 100° (bath)/0.1 mm. (*amide*, m.p. 101°, [α]_D¹⁶ +33° in MeOH, identical with 2:3:4:5-tetramethyl-*l*-arabonamide, m.p. 101°, [α]_D¹⁷ +34.0° in MeOH, from Ca *l*-arabonate with Me₂SO₄-NaOH and MeI-Ag₂O). (I) with Ba(OH)₂ affords isodimethylglucoscorbic acid, b.p. 230°/0.01 mm., [α]_D²⁰ ±0° in H₂O, converted by H₂SO₄-COMe₂ into (I), or by HCl-MeOH into (I) and 2-monomethylglucoscorbic acid. J. D. R.

Semi-micro-determination of hexuronic acids. W. VOSS and J. PFIRSCHKE (Ber., 1937, 70, [B], 631—634).—The substance (= about 50 mg. of lactone) is weighed into a flask containing a glass bead and two Pt tetrahedra. 10 c.c. of 20*M*-ZnCl₂ and about 0.5 g. of melted hard paraffin are added and, after the latter has solidified, the flask is connected with the condenser and gas burette. After 1 hr. the Hg level, barometric height, and temp. are determined. The liquid is heated to gentle boiling during 4 hr., after which it is allowed to cool until the paraffin has solidified (thus preventing back-diffusion of CO₂). After 1 hr. the above observations are repeated. A blank experiment is unnecessary. After addition of a const. correction dependent on the particular apparatus used, the variation between observed and calc. vals. is >0.2%. H. W.

Effect of iodine on rates of decomposition of formaldehyde, acetaldehyde, and propaldehyde.—See A., I, 314.

Formaldehyde from percarbonate.—See A., I, 321.

Kinetics of polymeric aldehydes. III. Physical influences on the rate of dissolution of polyoxymethylenes. J. LÖBERING (Ber., 1937, 70, [B], 665—668; cf. A., 1936, 1232, 1362).—The rate of dissolution of polyoxymethylenes (I) is not affected by the rate of stirring of the mixtures; hence diffusion is not concerned in the process and degradation does not occur in the solid crystal. This view is strengthened by the observation that the rate of dissolution is independent of the size of the particles. A definite solubility product must be assigned to (I), the long chains of which are depolymerised in solution. The determining factor is the rupture of C-O-C linkings in solution which is catalytically accelerated by H⁺ and OH⁻. H. W.

Absorbent for determination of acetaldehyde. J. V. RAKITIN (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 445—448).—The best conditions and a suitable apparatus for the most complete absorption of MeCHO in NaHSO₃ and for its titration are outlined.

P. W. C.

Production of nonaldehyde and nonyl alcohol. R. SHAGALOVA (Maslob. Shir. Delo, 1935, 11, 452—453).—An improved prep. from undecenoic acid is described. CH. ABS. (r)

Production of decaldehyde. O. OSIPOVA (Maslob. Shir. Delo, 1935, 11, 378—379).—A 70—75% yield is obtained by passing the mixed vapours of *n*-decoic and formic acids over MnO at 350—375°.

CH. ABS. (r)

Free radicals and atoms in primary photochemical processes. Dissociation of aliphatic ketones; the acetyl radical. H. H. GLAZEBROOK and T. G. PEARSON (J.C.S., 1937, 567—571; cf. A., 1935, 1211).—The relative quantities of radicals formed by the photolysis of COMe_2 , COMeEt , COMePr^a , COMePr^b , COMeBu^a , COPr^{a_2} , and COPr^{b_2} have been measured by the relative rates of interaction with Te. The radicals from the photolysis of COBu^a_2 could not be identified, but Me, Et, and Pr were absent. The products of photolysis of COMe_2 by ultra-violet light are Me and COMe . COMe radicals rapidly combine to Ac_2 , have a life of $<10^{-4}$ sec., are quantitatively decomposed by SiO_2 at 60° , and are removed at room temp., probably by dissociation to Me and CO. J. D. R.

Determination of acetone. C. O. HAUGHTON (Ind. Eng. Chem. [Anal.], 1937, 9, 167—168).—Messinger's CHI_3 method gives 102.5% COMe_2 with pure samples (the products containing about 0.6% of HCO_2H). The oxime reaction of Marasco (indicator, Me-orange-xylene-cyanol) is 97.1% complete. A. L.

Alkylation of ketones with sodamide. Propylation of ketones. I. N. NASAROV (Ber., 1937, 70, [B], 594—598).—The introduction of Me, Et, Pr^a , and Pr^b occurs in order of increasing difficulty. Addition of pinacolin to NaNH_2 in C_6H_6 followed by heating of the mixture until evolution of NH_3 ceases and gradual addition of Pr^aI gives $\beta\beta$ -dimethylheptan- γ -one, b.p. 168—172°, converted by further treatment with NaNH_2 and Pr^aI into $\beta\beta$ -dimethyl- δ -propylheptan- γ -one, b.p. 211—213°, and by NaNH_2 and MeI into $\beta\beta$ -trimethylheptan- γ -one, b.p. 178—181°. *iso*Butyryne, Pr^aI , and NaNH_2 in C_6H_6 give, according to conditions, $\beta\delta\delta$ -trimethylheptan- γ -one, b.p. 178—181°, or $\delta\delta\zeta$ -tetramethylnonan- ϵ -one, b.p. 229—232°. COPr^bBu^a is converted by Pr^aI into $\beta\delta\delta$ -tetramethylheptan- γ -one, b.p. 193—196°, but scarcely reacts with Pr^aI . $\beta\delta\delta$ -Tetramethylhexan- γ -one, b.p. 170—174°, is obtained from *isopropylpinacolin* or by two-fold methylation of COPr^bBu^a . Repeated methylation of COEtBu^a gives $\beta\delta\delta\epsilon$ -pentamethylhexan- γ -one, b.p. 195—197°. COEt_2 yields $\gamma\epsilon$ -dimethylheptan- δ -one, b.p. 170—173°, further ethylated to $\gamma\epsilon$ -dimethyl- γ -ethylheptan- δ -one, b.p. 204—207°. H. W.

Determination of acetylmethylcarbinol. A. F. LANGLYKKE and W. H. PETERSON (Ind. Eng. Chem. [Anal.], 1937, 9, 163—166).— $\text{CHAcMe}\cdot\text{OH}$ is fairly volatile from aq. solution, *k* (Virtanen and Pulkki, A., 1929, 140) being 1.3, reacts quantitatively with alkaline I, reduces CuSO_4 (Stiles *et al.*, J. Bact., 1926, 12, 427), requiring 2.95, and $\text{K}_3\text{Fe}(\text{CN})_6$ (Hagedorn and Jensen, A., 1923, ii, 265), requiring 2.67 equivs. of H per mol., and is oxidised quantitatively by $\text{K}_2\text{Cr}_2\text{O}_7$ to AcOH . It is best determined in fermented products by direct distillation, and analysis of the third quarter of the distillate with alkaline I. A. L.

Physalienone. P. KARRER and W. GUGELMANN (Helv. Chim. Acta, 1937, 20, 405—406).—Oxidation of physalien (zeaxanthin dipalmitate) with CrO_3 ($=40$) in C_6H_6 - AcOH gives physalienone $[\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}]_2\text{CH}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{C}_{15}\text{H}_{31})\cdot\text{CH}_2\text{Ac}]_2$, m.p. 144—145°, which closes resembles β -

carotenone in spectroscopic behaviour. It could not be hydrolysed satisfactorily with NaOEt . H. W.

Formation of carbohydrates by self-oxidation of hydrocarbons. N. A. ORLOV and A. T. SHALIGIN (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 341—343).—When O_2 is passed through $\text{CPh}_2\cdot\text{CH}_2$ (I) or $\text{CPhMe}\cdot\text{CH}_2$ (II) at 50° CH_2O and $(\text{CH}_2\text{O})_3$ can be detected in the H_2O through which the issuing gases are passed. Air saturated with (I) or (II) passed over Pt-Ni-Cr at 110° also gives CH_2O . The aq. extract of the product obtained by heating (I), diluted with sand and chalk, at 100 — 125° for 17 days gives positive tests for carbohydrates, and when (II) (64 g.) is similarly heated at 100 — 120° (50 days) the aq. extract contains 0.0231 g. of pentoses. J. W. B.

Determination of methoxyl in highly methylated carbohydrates. F. NEUMANN (Ber., 1937, 70, [B], 734—736).—The substance (3—5 mg.) is weighed in a glass container into a slightly modified Pregl micro-methoxy-apparatus in which CO_2 is led to the bottom of the flask. The temp. is raised gradually to $>80^\circ$ during 30 min. and maintained at this point until the sample is completely dissolved. It is then heated gradually during 30 min. to boiling; after a further 15 min. it is certain that MeI is completely driven into the receiver. The results agree closely with those required by theory. The lower results obtained when heating is rapid are attributed to the resinification of the methylated carbohydrate and consequent shielding of part of the OMe from the acid. H. W.

Formation of *l*-threose. K. IWADARE, S. FUKUNAGA, and B. KUBOTA (Bull. Chem. Soc. Japan, 1937, 12, 116—120).—*l*-Threose and its diacetamide have $[\alpha]_D^{20} +13.1^\circ$ and $+10.8^\circ$ (equilibrium) (cf. Deulofeu, A., 1936, 826). F. R. G.

Carbon dioxide formation on boiling cellular matter with sulphite. O. ROUTALA and T. VAUHKONEN (Suomen Kem., 1937, 10, B, 2).—On boiling Ca gluconate with SO_3 a pentose, probably arabinose, is formed and CO_2 is evolved. E. A. H. R.

Comparative action of magnesia on sugars and glucosides. (MLLE.) M. JOLY (J. Pharm. Chim., 1937, [viii], 25, 457—465).—Glucose (I) is entirely or almost entirely (98%) destroyed by MgO in hot H_2O or aq. EtOH ; three modifications of this method of removing (I) are detailed. Under similar conditions the following substances are destroyed to the extent stated: mannitol 27—60, fructose 80—98, sucrose 20—40, lactose 70—90, sorbitol 70—90, α -5—15, and β -methylglucoside 0%. R. S. C.

Determination of glucose by dichromate. S. M. STREPKOV (Biochem. Z., 1937, 290, 91—94).—The $\text{K}_4\text{Fe}(\text{CN})_6$ formed by interaction of the sugar with alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ is titrated with $\text{K}_2\text{Cr}_2\text{O}_7$ in acid solution using a solution of NHPh_2 in H_2SO_4 as indicator. The amount of $\text{K}_2\text{Cr}_2\text{O}_7$ used \propto the amount of glucose present, 1 mg. of glucose being $= 0.65$ c.c. of $0.05N\text{-K}_2\text{Cr}_2\text{O}_7$. P. W. C.

Formation of acetone [isopropylidene] derivatives of mercaptals. R. SUTRA (Compt. rend., 1937, 204, 783—785).—The rate of formation of diisopropylidene-*d*-glucose *Et*₂ mercaptal (I), $[\alpha]_{578}$

—48°, from COMe_2 and *d*-glucose Et_2 mercaptal with 0.1 and 0.01% of H_2SO_4 has been followed polarimetrically. The reaction is not of the first order. (I) is unstable and the $(\text{SEt})_2$ could not be eliminated without affecting the COMe_2 groups. In the similar formation of 2:3:5:6-diisopropylidene-*d*-mannose Et_2 mercaptal $[\alpha]_D$ passes through a min. val.

J. W. B.

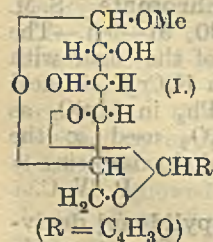
2:3:6-Trimethylglucose diethyl mercaptal. Its use in the preparation of 2:3:6-trimethylglucose. M. L. WOLFROM and L. W. GEORGES (J. Amer. Chem. Soc., 1937, 59, 601–603).—Methylcellulose and HCl (*d* 1.2) at 0–4° give 2:3:6-trimethylglucose, isolated as Et_2 mercaptal, m.p. 71–72°, $[\alpha]_D^{20} -15^\circ$ in CHCl_3 (4:5-dibenzoate, m.p. 115–116°, $[\alpha]_D^{20} +61^\circ$ in CHCl_3), readily hydrolysed to the pure S-free ether by $\text{Cd}(\text{CO}_3)_2\text{-MgCl}_2$. 2:3:4:6-Tetramethylglucose gives a Et_2 mercaptal, an oil (5-benzoate, m.p. 64–65°, $[\alpha]_D^{20} +33^\circ$ in CHCl_3).

R. S. C.

Transformation of hexoses into inositol. F. MICHEEL and H. RUKKOFF (Ber., 1937, 70, [B], 850–853; cf. A., 1935, 1225).—*d*-Galactose 6-*p*-toluenesulphonate is converted by ZnCl_2 and EtSH at 0° into *d*-galactose Et_2 mercaptal 6-*p*-toluenesulphonate, m.p. 115°, $[\alpha]_D^{20} +7.66^\circ$ in $\text{C}_5\text{H}_5\text{N}$, transformed by Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at 0° into *d*-galactose Et_2 mercaptal 2:3:4:5-tetra-acetate 6-*p*-toluenesulphonate, m.p. 111°, $[\alpha]_D^{20} +4.0^\circ$ in CHCl_3 , which with $\text{CaCO}_3\text{-HgCl}_2$ in COMe_2 affords al-*d*-galactose 2:3:4:5-tetra-acetate 6-*p*-toluenesulphonate (I), m.p. 140–141°, $[\alpha]_D^{20} -17.60^\circ$ in CHCl_3 {corresponding Et_2 acetal, m.p. 127° (decomp.), $[\alpha]_D^{20} -8.04^\circ$ to $+10.05^\circ$ in EtOH-CHCl_3 }. Condensation of (I) with $\text{Ac}_2\text{O-ZnCl}_2$ leads to *dl*-galactose hepta-acetate, m.p. 131°, thus confirming the mechanism of the transformation advanced previously (*loc. cit.*).

H. W.

Carbohydrates and furfuraldehyde. III. Reactions with α -methylgalactoside, sorbitol, and mannitol. H. BREDERECK and T. PAPADEMETRIU [with G. ROTHE] (Ber., 1937, 70, [B], 797–802; cf. A., 1936, 192).— α -Methylgalactoside is converted by CaCl_2 and furfuraldehyde containing a little HNO_3 (*d* 1.2) at 160–165°/100–150 mm. into 4:6-furylidene- α -methylgalactoside (I), m.p. 160–161°, $[\alpha]_D^{20} +157.6^\circ$ in H_2O . Its constitution follows from the following transitions. (I) is converted by $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ at room temp. into 4:6-furylidene- α -methylglucoside 2:3-diacetate, m.p. 125–126°, transformed by successive treatments with HCl-EtOH and $\text{CPh}_3\text{Cl-C}_5\text{H}_5\text{N}$ into 6-triphenylmethyl- α -methylgalactoside 2:3-diacetate, m.p. 85–87°, $[\alpha]_D^{20} +176.1^\circ$ in CHCl_3 , which gives the known 6-triphenylmethyl- α -methylgalactoside 2:3:4-triacetate, m.p. 179–181°. Alternatively, (I) is transformed by Ag_2O and MeI in COMe_2 into 4:6-furylidene-2:3-dimethyl- α -methylgalactoside, m.p. 138–140°, $[\alpha]_D^{20} +127.9^\circ$ in CHCl_3 , transformed by HCl-EtOH followed by $\text{CPh}_3\text{Cl-C}_5\text{H}_5\text{N}$ into



non-cryst. 2:3-dimethyl-6-triphenylmethyl- α -methylgalactoside. Sorbitol affords tri- (II), m.p. 186–

187°, $[\alpha]_D^{20} +19.7^\circ$ in CHCl_3 , and mono- (III), m.p. 192–193°, -furylidene- α -sorbitol. Hydrolysis of (II) with AcOH in boiling EtOH give difurylidene- α -sorbitol (IV), m.p. 202–203°. Since (III) gives a $(\text{CPh}_3)_2$ derivative, m.p. 222–224°, it is assumed in analogy with monobenzylidenesorbitol to be the 2:4 derivative. (IV), which gives a CPh_3 derivative, is possibly the 2:4-5:6 compound and (II) is the 1:3-2:4-5:6 derivative. Mannitol gives trifurylidene-mannitol, m.p. 176°, $[\alpha]_D^{18} -32.3^\circ$ in CHCl_3 , which could not be hydrolysed to the di-derivative, and furylidene-mannitol, m.p. 126°, $[\alpha]_D^{18} +19.0^\circ$ in H_2O ; the constitutions are not elucidated. H. W.

Ketone sugar series. VI. Effect of zinc chloride on ketose acetates. F. B. CRAMER and E. PACSU (J. Amer. Chem. Soc., 1937, 59, 711–715; cf. A., 1935, 1484).— ZnCl_2 in Ac_2O equilibrates α - and β -acetates in the ketose as in the aldose series. $[\alpha]$ below are $[\alpha]_D^{20}$ in CHCl_3 . Fructose α -, $[\alpha] +42.3^\circ$, and β -penta-acetate, $[\alpha] -122^\circ$, are equilibrated to a mixture, $[\alpha] -117^\circ$, from which both forms can be isolated. The second octa-acetate of turanose, $[\alpha] +106.5^\circ$ in Ac_2O , gives an equilibrium mixture, $[\alpha] +98^\circ$, from which a syrup, $[\alpha] +63^\circ$ in Ac_2O , is isolated; equilibration reconverts this into the mixture, $[\alpha] +98^\circ$; the existence of a new octa-acetate is inferred. The fourth turanose octa-acetate, $[\alpha] +103.2^\circ$ in Ac_2O , gives a mixture, $[\alpha] +40^\circ$, from which much of the first octa-acetate, $[\alpha] +19.6^\circ$, is obtained. $[\alpha]$ of β -acetobromofructose (I) in $\text{C}_5\text{H}_5\text{N}$ changes rapidly to -5.53° and then slowly to -45° ; with $\text{C}_5\text{H}_5\text{N}$ in EtOH a gel is transiently formed and the solution slowly acquires reducing properties. (I) and Ag_2O in MeOH give α - with much β -methylfructoside tetra-acetate. The relations of the acetates are discussed. R. S. C.

Reduction of α -*d*-glucoheptulose in presence of Raney's nickel. (MME.) Y. KHOUVINE (Compt. rend., 1937, 204, 983–984; cf. A., 1934, 513).— α -*d*-Glucoheptulose (I) is incompletely reduced (Na-Hg) in a slightly acid medium, but in an alkaline medium α -glucoheptitol (II) and α -glucoheptulitol are formed rapidly. *d*-Sorbitol with Raney Ni-H_2 in neutral or slightly alkaline solution affords *d*-sorbitol and *d*-iditol; the former reaction is slow. (I) with Raney Ni-H_2 in neutral or alkaline solution affords (II) and β -glucoheptitol completely.

J. L. D.

Attempts to synthesise sucrose. F. KLAGES and R. NIEMANN (Annalen, 1937, 529, 185–204).—All the theoretically possible, sterically indisputable methods of synthesising 1- α -glucosido-2- β -fructofuranose fail; some methods lead to β -glucosido- α -fructofuranose, and this is negative evidence that sucrose has the former structure. Acetoglucosidyl bromide (I), fructose tetrabenzoate (II), and $\text{Hg}(\text{OAc})_2$ do not react, (II) being inert. α -Glucose tetra-acetate, (II), and P_2O_5 even in complete absence of H_2O give $\beta\beta$ -trehalose octa-acetate with 12% of α -linkings, proving inversion of the tetra-acetate. α - or β -Glucose tetra-acetate (III) with $\text{EtBr-Ag}_2\text{CO}_3$ gives 75% of β - and 25% of α -ethylglucoside; fructose tetra-acetate gives mainly the α -form. (III) is converted into a 1:1 mixture of α - and

β -forms in C_6H_6 . (II), (III), and Ag_2CO_3 give 1.3% of a disaccharide octa-acetate, m.p. 178° , $[\alpha]_D^{20} +56^\circ$ in $CHCl_3$, formed entirely from (III), (II) being inert. (I) and $CH_2Ph\cdot OH$ in C_6H_6 give only the β -glucoside; acetofructosidyl halides give dextrorotatory benzylfructosides. Benzoylfructosidyl bromide, (III), and $Hg(OAc)_2$ do not react at 120° ; at 150° decomp. begins, and no disaccharide is formed. R. S. C.

Synthesis of flavin glucosides. R. KUHN and R. STRÖBELE (Ber., 1937, 70, [B], 747—752).—*d*-Arabinosido-2-nitro-4:5-dimethylanilide triacetate in MeOAc containing NEt_3 is reduced (PtO_2) and the filtered solution is treated with alloxan monohydrate and H_3BO_3 in AcOH, thereby giving 6:7-dimethyl-9-d-arabinosido-*flavin triacetate* (yield 60—65%), m.p. 240° (decomp.), $[\alpha]_D^{20} -453^\circ \pm 10^\circ$ in MeOAc, $[\alpha]_D^{20} -510^\circ \pm 15^\circ$ in 0.1N-NaOH, hydrolysed by NH_3 in abs. MeOH to 6:7-dimethyl-9-d-arabinosido-*flavin* ($+H_2O$), $[\alpha]_D^{20} -418^\circ \pm 5^\circ$ in C_5H_5N . 6:7-Dimethyl-9-l-arabinosido-*flavin triacetate*, m.p. 239° , $[\alpha]_D^{18} +440^\circ \pm 10^\circ$ in MeOAc, $[\alpha]_D^{22} +519^\circ \pm 15^\circ$ in 0.1N-NaOH, $[\alpha]_D^{22} +352^\circ \pm 15^\circ$ in 0.1N-NaOH + $Na_2B_4O_7$, readily hydrolysed by 0.1N-HCl, and 6:7-dimethyl-9-l-arabinosido-*flavin* are similarly obtained. 6:7-Dimethyl-9-dl-arabinosido-*flavin triacetate* has m.p. 260° . 6:7-Dimethyl-9-d-ribose-*flavin* (I), $[\alpha]_D^{20} +470^\circ \pm 15^\circ$ in C_5H_5N , gives a yellow solution with intense green fluorescence in H_2O . It is readily hydrolysed by cold dil. AcOH to *d*-ribose and 6:7-dimethylalloxazine and is very sensitive to 0.1N-NaOH. These flavin-9-glucosides are much more readily affected by light than is lactoflavin (II). (I) is reduced by $Na_2S_2O_4$ in neutral solution to a colourless leuco-compound which regenerates the pigment when shaken with air. Biologically it cannot replace (II); it does not promote growth in rats on a vitamin-B₂-free diet and does not give a catalytically active chromoprotein with the colloidal carrier of the yellow enzyme. H. W.

***o*-Nitroanilinoglucosides.** R. KUHN and R. STRÖBELE (Ber., 1937, 70, [B], 773—787).—The condensation products of *o*-NO₂-C₆H₄-NH₂ and 2-nitro-4:5-dimethylaniline with pentoses and hexoses are glucosides since they afford tri- and tetra-acetates, respectively, and not tetra- and penta-acetates, which would result from Schiff's bases. Since the pentosides afford CPh₃ derivatives they are furoid in structure and the pyranoid constitution is assumed but not proven for the hexosides. The condensation is greatly impeded by the presence of *o*-NO₂, but the difficulty is overcome by use of NH_4Cl (2—3%) as catalyst in boiling abs. EtOH. Free HCl and $NH_2Ph\cdot HCl$ cause decomp.; $NH_2Me\cdot HCl$ is about as active as NH_4Cl , but $NHMe_2\cdot HCl$ and $NMe_3\cdot HCl$ are less efficient. In all cases an equilibrium is attained and the yields are improved by using an excess of base or by chromatographic removal of the glucoside from the equilibrium mixture and treatment of the filtrate with more NH_4Cl ; yields then reach 80%. The m.p. of the glucosides are repeatable only under strictly defined conditions of crystallisation and desiccation, but they are readily characterised by their acetates. They are partly hydrolysed by hot H_2O , very readily by

acids. Reduction to the compounds $NH_2\cdot C_6H_2Me_2\cdot NH\cdot CH_2\cdot [CH\cdot OH]_n\cdot CH_2\cdot OH$ is effected in presence of Raney Ni, of Ni-Co-Cr, or of pure Ni, but for laboratory purposes the use of Pd-CaCO₃ or Pd-BaSO₄ is recommended since, although they are not the most efficient, they are most readily obtained with uniform properties. The most active catalyst is Pd(OH)₂, Zn(OH)₂, and Cu(OH)₂ on CaCO₃. The yields are greatly improved by use, during hydrogenation, of NaH₂BO₃, which forms complexes with the glucosides. The following compounds are described: 2-nitro-4:5-dimethylanilino-*d*-arabinose, softens at 111° (slight decomp.), $[\alpha]_D^{20} -20^\circ \pm 3^\circ$ in C_5H_5N , and its *triacetate*, m.p. 212° , $[\alpha]_D^{20} -137^\circ \pm 5^\circ$ in MeOAc; 2-nitro-4:5-dimethylanilino-*l*-arabinose (I), first modification, m.p. 111° , $[\alpha]_D^{18} +26^\circ \pm 3^\circ$ in C_5H_5N , and its *triacetate* (II), m.p. 212° , $[\alpha]_D^{20} +139^\circ \pm 5^\circ$ in MeOAc, second variety, m.p. 186° (decomp.), $[\alpha]_D^{20} +76.0^\circ \pm 1^\circ$ in C_5H_5N , converted by Ac_2O - C_5H_5N into (II); 2-nitro-4:5-dimethylanilino-*dl*-arabinose *triacetate*, m.p. 213 — 214° ; 2-nitro-4:5-dimethylanilino-*d*-ribose (III), m.p. 164° when cautiously heated, $[\alpha]_D^{20} +90^\circ \pm 3^\circ$ in C_5H_5N , and its *triacetate*, m.p. 163° , $[\alpha]_D^{20} +160^\circ \pm 5^\circ$ in MeOAc; *o*-nitroanilinoglucose, m.p. 70 — 75° , and its *tetraacetate*, m.p. 184° , $[\alpha]_D^{20} -75.2^\circ \pm 1^\circ$ in MeOAc; *o*-nitroanilino-*l*-arabinose, m.p. indef., and its *triacetate*, m.p. 151° , $[\alpha]_D^{20} +133.8^\circ \pm 1^\circ$ in MeOAc; *o*-nitroanilino-*d*-xylose *triacetate*, m.p. 149° , $[\alpha]_D^{21} -109.5^\circ \pm 2^\circ$ in MeOAc; 2-nitro-4:5-dimethylanilino-*d*-glucose, m.p. 214° (decomp.), $[\alpha]_D^{21} +11.7^\circ$ in C_5H_5N , and its *tetraacetate*, indef. m.p., $[\alpha]_D^{22} -65.1^\circ \pm 0.5^\circ$ in MeOAc; 2-nitro-4:5-dimethylanilino-*d*-mannose, indef. m.p., $[\alpha]_D^{20} -41.1^\circ \pm 1^\circ$ in MeOAc, its *tetraacetate*, m.p. 218° , $[\alpha]_D^{22} -93.8^\circ \pm 0.5^\circ$ in MeOAc, and *CPh₃* derivative, m.p. 130° (decomp.). The reduction of (I) and its subsequent condensation with alloxan and H_3BO_3 in AcOH to 6:7-dimethyl-9-l-araboflavin, m.p. 310° (decomp.), $[\alpha]_D^{25} -72.5^\circ \pm 2^\circ$ in 0.1N-NaOH, are described. (III) similarly affords lactoflavin (yield 60%) identical with the natural product. H. W.

Water-soluble polysaccharide from barley leaves. W. N. HAWORTH, E. L. HIRST, and R. R. LYNE (Biochem. J., 1937, 31, 786—788).—The polysaccharide extracted from barley leaves by cold H_2O gives a methylated derivative (OMe 43.0%), $[\alpha]_D^{20} -50^\circ$ in $CHCl_3$, which on hydrolysis yields 1:3:4-trimethylfructofuranose. It is constituted therefore of fructofuranose units linked together by bonds each of which engages the reducing group of one unit (C₂) and the C₆ position of the contiguous unit, and is closely related to if not identical with the lævan derived from the synthetic action of *B. mesentericus* (A., 1934, 760, 1338). Ketose determinations gave vals. equiv. to 93% of the total sugar and a small amount of a non-ketose sugar is probably present. The polysaccharide gives acetates of widely different rotations by varying the proportions of H_2O in the acetylation mixture; e.g., 0.25 g. in 0.5 ml. of H_2O with C_5H_5N (5 ml.) and Ac_2O (5 ml.) gave an acetate with $[\alpha]_D^{20} +11^\circ$ in $CHCl_3$, whereas with 1 ml. of H_2O the product had $[\alpha]_D^{20} -27^\circ$ in $CHCl_3$. P. W. C.

Polysaccharides. XXIII. Determination of the chain length of glycogen. W. N. HAWORTH, E. L. HIRST, and F. A. ISHERWOOD (J.C.S., 1937, 577—581).—Methylation (Me_2SO_4 -NaOH in COMe_2) of rabbit-liver glycogen, followed by hydrolysis (MeOH-HCl) and determination of the yields of tri- and tetra-methylmethylglucoside, indicates a chain length of 18 α -glucopyranose units linked in the 1:4 position. J. D. R.

"Terminal group" method of W. N. Haworth and H. Machemer with polysaccharides. K. HESS and F. NEUMANN (Ber., 1937, 70, [B], 710—721).—The cellulose acetate, sol. in COMe_2 , used as initial material by Haworth and Machemer (A., 1932, 1022) is unsuitable for the decision of the presence of ring or chain since during its prep. (treatment of cotton with $\text{Ac}_2\text{O-SO}_2\text{Cl}_2$ and subsequent partial removal of Ac by $\text{H}_2\text{O-H}_2\text{SO}_4$) some disintegration of the cellulose (I) is unavoidable and the products are not completely removed by the subsequent procedure. It is uncertain to what degree the terminal group content of (I) is affected by these impurities. A quant. separation of tetramethylmethylglucoside from the other methylated sugars is not possible by Haworth's method. Within limits there is an enrichment of the head fractions in Me_5 ether but considerable amounts remain in the intermediate fractions. These cannot be evaluated by OMe or n since less highly methylated materials are unavoidably present in addition to Me_4 ethers. H. W.

Detection of the smallest quantities of terminal groups in polysaccharides. F. NEUMANN and K. HESS (Ber., 1937, 70, [B], 721—727).—Attempts to separate permethylated (I) from incompletely methylated sugars by treatment of the latter with $p\text{-C}_6\text{H}_4\text{Me-SO}_2\text{Cl}_2$, BzCl , etc. followed by fractional distillation are unsatisfactory since the two classes of compound are not sufficiently dissimilar in properties and (I) is very firmly retained by the esters. The carbohydrate therefore is once methylated (apparatus described), whereby it acquires 42% OMe equiv. to complete etherification of about 72% of all the free OH of cellulose, and the % terminal group found is then applied to 72% of the initial material. Further methylation is considered inadvisable in view of probable simultaneous degradation. The methylated product is converted by 42% $\text{HCl-H}_2\text{O}$ into a mixture of methylated sugars transformed by 1% HCl-MeOH into the methylglucosides. The main portion of the less completely methylated sugars is removed by one or two fractional distillations. The glucosides are hydrolysed by 5% $\text{HCl-H}_2\text{O}$ with the object of removing most of the 2:3:6-trimethylglucose by crystallisation. The mother-liquor residues are treated with 1% HCl-MeOH and then successively with POCl_3 and $\text{C}_5\text{H}_5\text{N}$ and with Ba(OH)_2 . The salt is washed with Et_2O or light petroleum whereby (I) are removed. They are treated with Na in C_6H_6 and then distilled in a vac. ($\sim 10^{-3}$ mm.; bath temp. 40—60°) over Na and weighed (two types of apparatus described). *Ba* 2:3:6-trimethylmethylglucoside 4-phosphate has been prepared. The separation of synthetic mixtures of 2:3:6-trimethyl- and 2:3:4:6-tetramethyl-methylglucoside is described. H. W.

Cellulose. LV. The terminal group question and constitution of cellulose. K. HESS and F. NEUMANN (Ber., 1937, 70, [B], 728—733).—Application of the author's method of determining "terminal groups" to cellulose (I) of varied origin gives widely differing amounts of pentamethylglucose (II) if air is not excluded during the process. In the absence of air the formation of (II) could not be detected. Therefore either the mol. chain of (I) is so long that the formation of (II) is undetected (which necessitates the presence of many thousands of C_6 groups) or the mol. of (I) is cyclic and contains a completely unknown no. of units. The latter assumption is the more probable. H. W.

Triphenylmethyl ether of cellulose. P. P. SCHORIGIN, A. E. VEITZMAN, and N. N. MAKAROVA-ZEMLIANSKAJA (J. Gen. Chem. Russ., 1937, 7, 430—439).—Cellulose 6-CPh₃ ether does not combine with Na or CS_2 ; it gives a Me_1 ether with Me_2SO_4 in aq. NaOH, or with MeI and Ag_2O , whilst further methylation leads to replacement of CPh₃ by Me. An attempted prep. of cellulose 6-triphenylmethyl 2:3-dimethyl ether from the 2:3-Me₂ ether was unsuccessful. Sakaruda's results (A., 1935, 201) were confirmed. R. T.

Werner complexes. Substitutions in optically active chlorinated complexes.—See A., I, 322.

Preparation of diacetylenediamine. L. H. AMUNDSEN (J. Chem. Educ., 1937, 14, 141—142).—Details of the prep. from 60—70% $(\text{CH}_2\text{-NH}_2)_2$ and glacial AcOH are given. L. S. T.

Aliphatic polyamines. IV. J. VAN ALPHEN (Rec. trav. chim., 1937, 56, 343—350; cf. A., 1936, 1274).—Interaction of $\text{CH}_2(\text{CH}_2\text{Br})_2$ and $(\text{CH}_2\text{-NH}_2)_2\text{H}_2\text{O}$ (cf. A., 1936, 1493) affords *NN'*-di- β' -aminoethylpropylene- $\alpha\gamma$ -diamine, *NN'*-di- γ' -(β' -aminoethyl)aminopropylethylenediamine (I), b.p. 252°/14 mm. (hydrochloride, m.p. 275°; *H* oxalate, m.p. 235°; *picrate*, m.p. 220°, and *phenylthiocarbamide*, m.p. 135—140°), a fraction, b.p. 316°/14 mm., which contains a little *di-β'-(γ'-β''-aminoethylamino-propyl)aminoethylpropylene-αγ-diamine* (isolated as the hydrochloride, m.p. >300°, of its *dibenzyl* derivative), but is mainly 1:4:8:11-tetra-azacyclotetradecane, $[\text{CH}_2]_{12} \begin{smallmatrix} \text{NH} \cdot [\text{CH}_2]_3 \cdot \text{NH} \\ | \quad \quad | \\ \text{NH} \cdot [\text{CH}_2]_3 \cdot \text{NH} \end{smallmatrix} [\text{CH}_2]_2$ (II), b.p. 316°/14 mm. [*picrate*, decomp. 210°; *H* oxalate, decomp. 221°; *phenylthiocarbamide*, decomp. 138—140°; *hydrochloride* (+1H₂O); and *nitrate*, m.p. 205° (decomp.)], and fractions, b.p. 244°/16 mm. and 275°/16 mm., which probably resemble (II) in structure. With CS_2 in EtOH (I) gives an amorphous product converted by heat into 1:3-di-(γ -1'-thiotetrahydroglyoxalyl)-propylthiotetrahydroglyoxaline, m.p. 166—167°, and with PhCHO in EtOH containing dissolving Na (I) affords the CH_2Ph derivative [+2H₂O, m.p. 54°; *hydrochloride*, m.p. >300° (decomp.); *nitrate*, m.p. 211°; *picrate*, m.p. 211°, and (*NO*)₆-derivative, m.p. 86°]. J. L. D.

Halogeno-salts of rhodium.—See A., I, 322.

Separation of choline and ethanolamine. E. CHARGAFF (J. Biol. Chem., 1937, 118, 417—419).—Mixed hydrochlorides of choline (I) and ethanolamine

(II) in H_2O are treated with $NaHCO_3$ and $CHCl_3$, and $CH_3Ph \cdot O \cdot COCl$ is added, followed after 1 hr. by HCl . (I) can then be determined in the H_2O layer (as enneaidide, aurichloride, platinichloride, or perchlorate), and from the $CHCl_3$ carbobenzyloxy-ethanolamide, m.p. 66.5° , be isolated, and converted into (II) (aurichloride) by $Pd-H_2$ reduction.

E. W. W.

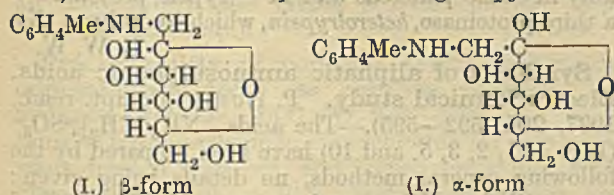
Methylcholines. Oxidation with permanganate. E. KAHANE (Bull. Soc. chim., 1937, [v], 4, 717—727).—Oxidation of choline perchlorate with $0.1N-KMnO_4$ (1.45 atoms of O) in presence of 1—2 c.c. of 10% H_2SO_4 at room temp. affords betaine (I), and α -methylcholine chloride (II) similarly takes up 1.68 atoms of O to give $+NMe_3 \cdot CHMe \cdot CO_2^-$. Under these conditions the chlorides of β -methylcholine (III), its Ac derivative, and acetylcholine are unattacked, although in more strongly acid solution (III) absorbs 5 O to give (I). By use of this method it is found that the products obtained by the action of NMe_3 on chloropropyl alcohols obtained in various ways are all essentially the same and contain only 5—6% of (II).

J. W. B.

Isolation of glucosamine. E. CHARGAFF and M. BOVARNICK (J. Biol. Chem., 1937, 118, 421—426).—Aq. glucosamine hydrochloride (I) with $NaHCO_3$ and $CH_3Ph \cdot O \cdot COCl$ (II) gives carbobenzyloxyglucosamide, m.p. 214° (decomp.) (corr.), $[\alpha]_D^{24} +62.8^\circ \rightarrow +75.4^\circ$ in C_5H_5N , which with $Pd-H_2$ yields 93% of the original (I). (II) does not give insol. derivatives with *l*-arabinose, *d*-ribose, *d*-xylose, *d*-glucose, *d*-mannose, *d*-galactose, *d*-fructose, or glucuronogalactose, and may therefore be used to separate (I) from these sugars; a method of separation from mixed sugars, and the identification of the latter in the residue, are described. (II) may be used to separate (I) from glycine, as the carbobenzyloxy-derivative of the latter is not pptd. until HCl is added.

E. W. W.

The Amadori transformation. R. KUHN and F. WEYGAND (Ber., 1937, 20, [B], 769—772; cf. A., 1936, 1095).—The product of the isomerisation (Amadori, A., 1926, 60; 1929, 429; 1931, 1039, 1049) of the labile *p*-toluidino-*d*-glucopyranoside



is identified as *N*-*p*-tolyl-*d*-isoglucosamine (I). It shows marked mutarotation in C_5H_5N and when oxidised with CrO_3 gives 0.6 mol. of $AcOH$. It is a very powerful reducing agent resembling ascorbic acid in its conversion of $o\text{-}C_6H_4(NO_2)_2$ in alcoholic alkaline solution into $o\text{-}NO_2 \cdot C_6H_4 \cdot NH \cdot OH$. It is remarkably stable to HCl , which does not induce simple hydrolysis. It yields an oxime, m.p. $135\text{—}136^\circ$, $[\alpha]_D^{19.5} -21^\circ$ in C_5H_5N . It is reduced to *N*-*p*-tolyl-*d*-mannamine, m.p. $194\text{—}195^\circ$, $[\alpha]_D^{21} +28.8^\circ$ in C_5H_5N , also obtained by condensing *p*- $C_6H_4Me \cdot NH_2$ with mannose in boiling $EtOH$ containing NH_4Cl to *p*-toluidino-*d*-mannoside, m.p. 184° , $[\alpha]_D^{20} -181^\circ$ in C_5H_5N , and hydro-

genation of the latter. The Amadori isomerisation affords a new transition from the *d*-glucose to the *d*-fructose series.

H. W.

Chemical comparison between chitin and cellulose. K. H. MEYER and H. WEHRLI (Helv. Chim. Acta, 1937, 20, 353—362).—Chitin (I) undergoes slight deacetylation during its prep. by treatment of the shells of crustaceæ with dil. $NaOH$ followed by dil. HCl and finally by $EtOH$. It has Cu no. 1.5. Determinations of the mol. wt. of (I) by osmotic measurements is impossible since it is decomposed by long contact with available solvents but measurements of viscosity indicate a val. comparable with that of cellulose (II) derived from wood by chemical methods. The heat of activation of the acidic hydrolysis of (I) is practically identical with that of (II) and in good agreement with the presence of the same type of β -linkings in (I) and (II). (I) is sol. only in mineral acids, in which it becomes degraded, and is unaffected by the mineral solvents of (II). A process comparable with mercerisation is not observed with (I). Esterification of (I) is much more difficult than that of (II). Prolonged treatment of (I) with conc. $NaOH$ causes almost complete elimination of Ac , giving a polyglucosamine (III) which according to Cu no. and viscosity contains about 25 sugar residues. The corresponding hydrochloride, although cryst., is derived from a complex base which is thus analogous to the oligosaccharide obtained by degradation of cellulose acetate. Deamination of (III) under very mild conditions gives a substance of low mol. wt. which yields glucosephenylosazone with $NHPh \cdot NH_2$; transformation of NH_2 into OH is thus accompanied by hydrolysis of the glucosidic linking.

H. W.

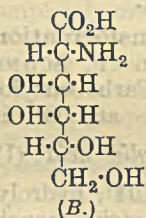
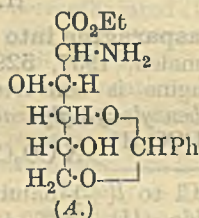
Transformation of *l*(-)-asparagine into *l*(-)-serine. F. SCHNEIDER (Annalen, 1937, 529, 1—10).—Carbobenzyloxy-*l*-asparagine is converted by $NaOCl$ at 60° into carbobenzyloxy-*l*-glyoxalidone-carboxylic acid (I), $CH_2 \cdot CH(CO_2H) > N \cdot CO_2CH_2Ph$, m.p. 194° , hydrolysed by HCl to *l*(+)-diaminopropionic acid monohydrochloride (II), $[\alpha]_D^{20} +25.25^\circ \pm 0.2^\circ$ in *N*- HCl . (I) is transformed by H_2 in presence of Pd -sponge into *l*(-)-glyoxalidone-2-carboxylic acid, m.p. $190\text{—}191^\circ$ (decomp.), $[\alpha]_D^{19} -16.0^\circ \pm 0.2^\circ$. (II), $ClCO_2CH_2Ph$, and KOH afford *l*- $\alpha\beta$ -dicarbobenzyloxamidopropionic acid, m.p. $99\text{—}100^\circ$, converted by PCl_5 in $CHCl_3$ into the corresponding anhydride, which is transformed by $5N\text{-}HCl\text{-}MeOH$ into *Me l*- α -amino- β -carbobenzyloxamidopropionate hydrochloride, m.p. 164° . This is converted by $BzCl\text{-}MgO$ in $H_2O\text{-}CHCl_3$ into *Me l*- α -benzamido- β -carbobenzyloxamidopropionate, m.p. 102° , hydrogenated (Pd -sponge) to *Me l*- β -amino- α -benzamidopropionate hydrochloride, m.p. 179° (decomp.), which is transformed by the successive action of $Ba(NO_3)_2\text{-}HCl$ and 16% HBr at 140° into *l*(-)-serine, $[\alpha]_D^{20} -7.20^\circ \pm 0.25^\circ$ in H_2O , $+14.75^\circ \pm 0.30^\circ$ in $H_2O + N\text{-}HCl$. *l*(-)-Asparagine, *l*(+)- $\alpha\beta$ -diaminopropionic acid, and *l*(-)-serine are therefore configuratively related.

H. W.

Constitution of the copper salts of aspartic and glutamic acids. P. PFEIFFER and H. WERNER

(Z. physiol. Chem., 1937, 246, 212—218).—Aq. Cu aspartate (I), $(C_4H_5O_4N)_2Cu \cdot 9H_2O$ (1 mol.), with dil. NaOH (<2 mols.) affords $Cu(OH)_2$ and a blue-violet solution containing a substance (pptd. by EtOH) with Cu : Na : N = 1 : 2 : 2, also yielded by (I) + Na aspartate [corresponding Ba salt prepared from (I) + Ba aspartate]. Hence (I) is $[Cu(C_4H_5O_4N)_2]Cu$ whilst parallel reactions indicate Cu glutamate to be $[Cu(C_5H_7O_4N)_2]Cu$. Structural formulæ for the two complex salts are suggested. F. O. H.

New degradation of glucosamic acid. Configuration of glucosamic and chondrosamic acid. P. KARRER and J. MAYER (Helv. Chim. Acta, 1937, 20, 407—417).—Et benzylideneglucosamate hydrochloride is transformed by NaOH and $ClCO_2Et \cdot Na_2CO_3$ into the N-carbethoxy-derivative (I), m.p. 129°, which is oxidised by $Pb(OAc)_4$ in C_6H_6 to Et carbethoxyaminohydroxyacetate, $CO_2Et \cdot NH \cdot CH(OH) \cdot CO_2Et$, m.p. 87° (transformed by $p\text{-NO}_2 \cdot C_6H_4 \cdot NH \cdot NH_2$ or $NH_2 \cdot CO \cdot NH \cdot NH_2$ into the p-nitrophenylhydrazone and semicarbazone, respectively, of glyoxylic acid and oxidised by I to $H_2C_2O_4$). Benzylideneglucosamic acid does not therefore contain free OH at $C_{(3)}$ and $C_{(4)}$. Since its Et ester (II) is transformed by Ac_2O in C_5H_5N into a Ac_3 derivative, m.p. 115°, which after removal of $:CHPh$ with 60% AcOH does not give CH_2O when oxidised by HIO_4 it follows that a compound with free OH groups at $C_{(5)}$ and $C_{(6)}$ is not thus formed, and the modified constitution (A) is assigned to (II). The fission of (I) establishes the possibility of the degradation of NH_2 -alcohols by $Pb(OAc)_4$ which in this instance does not appear to be facilitated by the presence of OH and NH_2 in the cis position to



one another. The behaviour of glucosamic dipeptide to dipeptidase indicates the d-glucose configuration with NH_2 and OH at $C_{(2)}$ and $C_{(3)}$ in the trans position in glucosamic acid. Confirmation is obtained from the rotation dispersion and Cotton effect of Cu glucosamate, which assign it to the d- NH_2 -acid series. The analogous behaviour of Cu chondrosamate indicates the configuration (B) for chondrosamic acid (III). (III) or its ester could not be caused to react with PhCHO or $p\text{-NO}_2 \cdot C_6H_4 \cdot CHO$ but treatment of (III) in NaOH with Ac_2O yields N-acetylchondrosamolactone, m.p. 165°, which does not afford a $:CHPh$ compound but is transformed by 1% HCl-COMe₂ into N-acetylisopropylidenechondrosamolactone, m.p. 164°. H. W.

Proteolytic enzymes. XIII. Synthetic substrates for chymotrypsin. M. BERGMANN and J. S. FRUTON (J. Biol. Chem., 1937, 118, 405—415).—Cryst. chymotrypsin (I) hydrolyses carbobenzyloxyglycyl-L-tyrosylglycineamide (II), m.p. 192°, obtained by hydrogenating N-carbobenzyloxy-O-acetyl-L-

tyrosylglycine Et ester (III), m.p. 127° (from the L-tyrosyl chloride and $NH_2 \cdot CH_2 \cdot CO_2Et$); one peptide linking is broken, giving carbobenzyloxyglycyl-L-tyrosine, further hydrolysed by cryst. carboxypeptidase to tyrosine (cf. animal digestion of proteins). [For further hydrolyses by (I), see below.] Papain-HCN hydrolyses (II) to carbobenzyloxyglycine and L-tyrosylglycine. (II) is hydrogenated to glycyl-L-tyrosylglycineamide hydrochloride (IV), m.p. 89—90°. (III) is converted by $NH_3 \cdot MeOH$ into carbobenzyloxy-L-tyrosylglycineamide (V), m.p. 116°, which with (I) gives N-carbobenzyloxytyrosine (an oil). With MeOH-NaOH, (III) gives carbobenzyloxy-L-tyrosylglycine (VI), m.p. 100°. Tyrosine Et ester with carbobenzyloxyglycyl chloride yields carbobenzyloxyglycyl-L-tyrosine Et ester, m.p. 118°, hydrolysed by NaOH to carbobenzyloxyglycyl-L-tyrosine, m.p. 107°. Carbobenzyloxy-L-tyrosine Et ester with $N_2H_4 \cdot H_2O$ forms carbobenzyloxy-L-tyrosylhydrazide, m.p. 220°; this with $NaNO_2 \cdot HCl$ forms the azide, which with glycylglycine Et ester yields carbobenzyloxy-L-tyrosylglycylglycine Et ester, m.p. 165°, converted by $NH_3 \cdot MeOH$ into the amide (VII), m.p. 218°. Carbobenzyloxy-L-phenylalanyl chloride and glycine Et ester form carbobenzyloxy-L-phenylalanylglycine Et ester, m.p. 111°, which on hydrogenation and treatment with carbobenzyloxyglycyl chloride gives carbobenzyloxyglycyl-L-phenylalanylglycineamide (VIII), m.p. 178°. Carbobenzyloxyglycyl-L-glutamylglycineamide (IX), obtained from the ester, has m.p. 175°.

(IV) and (V) are readily hydrolysed by (I), (VII) and (VIII) much more slowly; (VI) and (IX), and benzoylglycyl-L-lysineamide (X), carbobenzyloxyglycyl-L-leucylglycineamide, benzoyl-L-leucyl-L-leucylglycine, and chloroacetyltyrosine are not attacked. From the above, (I) is shown to be a peptidase, i.e., proteinases are endopeptidases (cf. A., 1936, 1152). That (I) distinguishes between phenylalanyl and leucyl, and similar differentiations, must depend not on combination of enzyme with side-chain, but on the effect of the latter on the sensitivity of internal peptide linkings. Since (X) is not hydrolysed by (I), or by cryst. trypsin, separately or mixed, there is probably in cattle pancreas and in "tryptic proteinase" a third proteinase, heterotrypsin, which hydrolyses (X).

E. W. W.

Synthesis of aliphatic aminosulphonic acids. Electrochemical study. P. RUMPF (Compt. rend., 1937, 204, 592—595).—The acids $^+NH_3 \cdot [CH_2]_n \cdot SO_3^-$ (I) ($n = 1, 2, 3, 5$, and 10) have been prepared by the following general methods, no details being given: (a) $(CH_2)_m > NH$ and aq. H_2SO_3 afford $NH_2 \cdot [CH_2]_m \cdot SO_3H$ when $m = 2$ or 3; (b) action of NH_3 on γ -chloro-n-propane- α -sulphonyl chloride, b.p. 124—127°/15 mm. (from $OH \cdot [CH_2]_3 \cdot SO_3Na$); (c) by the action of conc. aq. Na_2SO_3 on halogenoalkylphthalimides and hydrolysis of the sulphonated amides so obtained; thus $NHBz \cdot [CH_2]_4 \cdot CH_2Cl$ gives ϵ -amino-n-pentane- α -sulphonic acid, m.p. approx. 310°, and $o\text{-C}_6H_4(CO)_2N \cdot [CH_2]_3Br$ affords γ -amino-n-propane- α -sulphonic acid; (d) from β -, γ -, or δ -sulphoacids by conversion of CO_2H into NH_2 with N_2H_4 -conc. $H_2SO_4 \cdot CHCl_3$ at 45°; thus γ -bromoundecic acid is converted through the γ - SO_3H derivative into γ -amino-n-decane- α -sulphonic acid, m.p. approx.

340° (decomp.) (block). The vals. of $-\log K_{\text{H}}$ for (I), determined by electrometric titration of 0.1N solution with *N*-NaOH using a glass electrode, are approx. 1, 5.75 (± 0.05), 9.30, 10.05, 10.95, and 11.35 (± 0.2) when $n = 0, 1, 2, 3, 5$, and 10, respectively, and approx. 5.8 and 1.4 for $^+\text{NH}_3\cdot\text{CHMe}\cdot\text{SO}_3^-$ and $^+\text{NH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{SO}_3^-$, respectively.

J. W. B.

Synthesis of α -glutamylcysteinylglycine (isoglutathione). V. DU VIGNEAUD, H. S. LORING, and G. L. MILLER (J. Biol. Chem., 1937, 118, 391—395).—*S*-Benzylcysteinylglycine (A., 1935, 1486) and carbobenzyloxyglutamic anhydride in $\text{C}_5\text{H}_5\text{N}$ give *N*-carbobenzyloxy- α -glutamyl-*S*-benzylcysteinylglycine, m.p. 191—192°, which is also obtained from γ -Et *N*-carbobenzyloxyglutamate (A., 1933, 1039, 1281) by conversion into the acid chloride and combination with *S*-benzylcysteinylglycine Me ester, and which with Na in liquid NH_3 yields α -glutamylcysteinylglycine (isoglutathione), m.p. 152—153° (decomp.), $[\alpha]_D^{25} + 2.5^\circ$ in H_2O .

E. W. W.

Selenium-substituted amino-acids. II. Optically active forms of selenocystine. A. FREDGA (Svensk Kem. Tidskr., 1937, 49, 124—130; cf. A., 1936, 1096).—(+)-Selenocystine (I), m.p. about 215° (decomp.) after softening at 180°, $[M]_D^{25} + 573^\circ$ in 0.5N-HCl (hydrochloride), has been obtained from *D*-serine. (+)-Selenocystine has $[M]_D^{25} - 571^\circ$. An active racemate of (I) and (—)-cystine and its hydrochloride are described.

M. H. M. A.

Catalytic hydrogenation of amides of α -hydroxy-acids. H. ŌEDA (Bull. Chem. Soc. Japan, 1937, 12, 121—127).—*dl*-OH·CHMe·CO·NH₂ (A., 1936, 1092) was hydrogenated (A., 1935, 189) to OH·CHMe·CH₂·OH, $\alpha\delta$ -diamino- $\beta\gamma$ -dimethylbutane [picrate, decomp. $> 260^\circ$; Bz₂ derivative, m.p. 227—228° (corr.)] and its *N*-Pr derivative (picrate, m.p. about 238°; platinichloride, decomp. 265—270°). Similarly *l*-OH·CHBu ^{δ} ·CH₂·OH, *dl*- $\alpha\delta$ -diamino- $\beta\gamma$ -diisobutylbutane, m.p. 62—64° [hydrochloride, decomp. $> 330^\circ$; picrate, decomp. 248°; Bz₂ derivative, m.p. 223—224° (corr.); platinichloride, decomp. $> 330^\circ$], and an unidentified base giving a hydrochloride, m.p. 220—230° (decomp.).

F. R. G.

Precipitability of complex trithiocarbamide cuprochloride from its aqueous solution. E. STORFER (Monatsh., 1937, 70, 236—250).—Aq. solutions of trithiocarbamide cuprochloride (I) give ppts. when treated with org. and inorg. compounds with dissociation const. $> 10^{-3}$; certain exceptions are recorded. The upper and lower limits of concn. of uni-, bi-, ter-, and quadri-valent ions required for the pptn. of (I) from H_2O and the "breadth of zone" are recorded. The compounds $\text{C}_5\text{H}_{24}\text{O}_6\text{N}_{10}\text{S}_6\text{Cu}_2$, $\text{C}_5\text{H}_{24}\text{O}_6\text{N}_{10}\text{S}_6\text{Cu}_2$, $\text{C}_8\text{H}_{28}\text{O}_6\text{N}_{12}\text{S}_6\text{Cu}_2$, $\text{C}_9\text{H}_{16}\text{O}_2\text{N}_{12}\text{S}_3\text{Cu}_3\text{Fe}$, and $\text{C}_{10}\text{H}_{22}\text{O}_3\text{N}_{14}\text{S}_4\text{Cu}_4\text{Fe}$ are obtained by adding K_2SO_4 , CuSO_4 , $\text{K}_2\text{C}_2\text{O}_4$, $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ respectively to aq. solutions of (I).

H. W.

Crystalline compound of semicarbazide and semicarbazide hydrochloride. H. L. HALLER and F. B. LaFORGE (J. Amer. Chem. Soc., 1937, 59, 760).—Semicarbazide hydrochloride (I) and

$\text{C}_5\text{H}_5\text{N}$ in aq. EtOH give a 1:1 additive compound, m.p. 132°, of (I) and semicarbazide. This may be formed when semicarbazides are prepared by $\text{C}_5\text{H}_5\text{N}$. With conc. HCl it gives (I).

R. S. C.

Effect of certain substances on the formation of hydrocyanic acid by the oxidation of fructose or alloxan with ammoniacal copper salts. J. PAROD (Compt. rend., 1937, 204, 871—873; cf. A., 1936, 968).—Fructose (I) and alloxan (II) with $\text{NH}_3\text{-Cu}(\text{OH})_2$ in different solvents at 60° afford HCN. (II) gives the greater yield when dissolved in many mono- and di-carboxylic acids, and polyhydric alcohols. In H_2SO_3 , (I) is the better source, and liberates more HCN the more prolonged is the reaction. When glycerol is the solvent, a rapid, initial reaction alone occurs. (II) liberates HCN throughout the duration of the reaction in either solvent.

J. L. D.

Additive products of hydrocyanic acid with glucosylarylamines and glucosylpiperidines. E. VOTOČEK and O. WICHTERLE (Coll. Czech. Chem. Comm., 1937, 9, 109—119).—Compounds of type $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_n\cdot\text{CH}(\text{NHR})\cdot\text{CN}$ are prepared from the reaction products of sugars and NH_2Ph . The product from *l*-arabinose gives, with anhyd. HCN in EtOH, anilino-*l*-arabohexonitrile, m.p. 150° (decomp.), $[\alpha]_D - 157^\circ$ (all rotations in MeOH). *d*-Xylosylaniline, m.p. 148°, $[\alpha]_D$ (extrapolated) -79.6° , falling to -24° , gives anilino-*d*-xylohexonitrile, m.p. 115—120°. The product from rhamnose and NH_2Ph gives anilino-*l*-rhamnohexonitrile, m.p. 143°, $[\alpha]_D - 34.5^\circ$. *l*-Fucosylaniline, m.p. 150—151°, $[\alpha]_D$ (extrapolated) $+102^\circ$, falling to $+49^\circ$, yields anilino-*l*-fucohexonitrile, m.p. 173—174° (decomp.), $[\alpha]_D + 156^\circ$. Mannosylaniline (simplified prep. from vegetable ivory) gives anilino-*d*-mannoheptonitrile, $[\alpha]_D + 156^\circ$. The reaction products from piperidine with rhamnose and with mannose give respectively piperidyl-*l*-rhamnohexono-, m.p. 142—143°, $[\alpha]_D + 27^\circ$, and *d*-mannoheptononitrile, m.p. 125—127° (decomp.), $[\alpha]_D - 10^\circ$. Anilino-glucosylheptonitrile with $\text{Ac}_2\text{O-NaOAc}$ gives an Ac_5 derivative, and anilino-galactoheptonitrile an Ac_5 derivative, m.p. 122°. Glucose and *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ yield *d*-glucosyl-*m*-nitroaniline, m.p. 172—186°, unchanged by HCN.

E. W. W.

Esterification of hydrocobalticyanic acid with diazomethane. J. MEYER and O. RAMPOLDT (Z. anorg. Chem., 1937, 232, 188—192).—In MeOH the reaction yields about 40% of $\beta\text{-Me}_3\text{Co}(\text{CN})_6$. An incompletely methylated ester is also formed.

E. S. H.

Carbon rings. XXXI. Relationships between m.p. and density in aliphatic and cyclic homologous series. L. RUZICKA and G. GIACOMELLO (Helv. Chim. Acta, 1937, 20, 548—562).—Calculation of *d* for cyclic ketones between 120° and -80° shows that at the latter temp. a max. is not observed for the 10-membered ring. With increasing temp. the max. becomes gradually apparent and is very pronounced at 120°. There appears no reason to connect max. *d* with min. yield and it is doubtful whether general conclusions can be based on the val. of *d* at an arbitrarily chosen, fixed temp. The question of corresponding temp. is discussed and $20^\circ > \text{m.p.}$ is chosen

in order to avoid undue departure from observed vals. Tables are given for d of n -paraffins, cyclic hydrocarbons, n -aldehydes and n -ketones, cyclic ketones, and diketones, lactones, polymethylene carbonates and dicarboxylic esters, and cyclic imines under this condition. The qual. course of the graphs is readily understood if it is assumed that the arrangement of the mols. in the liquid state is mainly conditioned by the no. of mols. in the unit of vol. and the probability of as close a packing of the mols. as possible; the resultant of these factors represents d . The close similarity of the graphs of aliphatic and cyclic compounds indicates that polymembered rings with an even no. of members are to be regarded as two halves of a 6-ring joined by two approx. parallel chains of CH_2 groups. Rings with an odd no. of members are represented as the two "halves" of a 5-ring formed in the same manner as shown above. Practical justification for the use of a corresponding temp. is afforded by the regularities between d and m.p. which then become obvious in a homologous series. H. W.

Aromatisation of certain homologues of cyclopentane and of paraffins in presence of platinised charcoal. B. A. KAZANSKI and A. F. PLATE (J. Gen. Chem. Russ., 1937, 7, 328—334).—The following products are obtained by passing the hydrocarbons over Pt-C at 310—315°: δ -methyloctane and o - $\text{C}_6\text{H}_4\text{MeEt}$ from n -butylcyclopentane; p -xylene from Bu^n ; PhEt and o -xylene from n -octane; m - $\text{C}_6\text{H}_4\text{MePr}^s$ from diisomyl. R. T.

Equilibrium and kinetics of diene synthesis.—See A., I, 313.

Autoxidation of cyclic ethylenic hydrocarbons. II. R. DUPONT (Bull. Soc. chim. Belg., 1937, 46, 21—26; cf. A., 1936, 712).—Autoxidation of 1:2-dimethyl- Δ^1 -cyclohexene at 70° for a week, followed by treatment with $\text{Ba}(\text{OH})_2$ and distillation at 18 mm., yields chiefly 1:2-dimethyl- Δ^1 -cyclohexen-3-one (semicarbazone, m.p. 224°) and *trans*-1:2-dimethylcyclohexane-1:2-diol [oxidised to the ketone (semicarbazone, m.p. 223°)], with a little $\text{Ac}[\text{CH}_2]_4\text{Ac}$.

A. Li.

Contact transformation of Δ^2 -butenylcyclohexane (δ -cyclohexyl- Δ^2 -butene). R. J. LEVINA and M. I. TSCHERNIAK (J. Gen. Chem. Russ., 1937, 7, 402—404).— δ -cyclohexyl- Δ^2 -butene yields PhBu^a and n -butylcyclohexane when passed over Pt-C at 210° in CO_2 . R. T.

Catalytic transformation of cyclohexylacetylene. R. J. LEVINA and A. A. POTANOVA (J. Gen. Chem. Russ., 1937, 7, 353—356).—cyclohexylacetylene yields PhEt and ethylcyclohexane when passed over Pt-C at 200°. R. T.

cycloHeptane and hydrogenation-dehydrogenation catalysis. M. B. TUROVA-POLLAK (J. Gen. Chem. Russ., 1937, 7, 369—371).—cycloHeptane is gradually converted into methylcyclohexane, and this into PhMe, by repeated passage over Pt-C at 300—315°. R. T.

cycloHexylcyclopentane and its transformations during hydrogenation-dehydrogenation catalysis. S. I. CHROMOV (J. Gen. Chem. Russ.,

1937, 7, 350—352).—The products obtained with H_2 at 300—310° (Pt-C catalyst) were CHPhEt_2 and α - and β -phenylpentane. R. T.

Isomerisation of dicyclohexyl in presence of aluminium chloride. R. J. LEVINA, J. K. JURIEV, and A. I. LOSCHKOMOINIKOV (J. Gen. Chem. Russ., 1937, 7, 341—349).—Dicyclohexyl and AlCl_3 at 100° (50 hr.) yield chiefly *trans-trans*-dicyclohexyl, b.p. 217—219°, from which 2:6- $\text{C}_{10}\text{H}_8\text{Me}_2$ is obtained by dehydrogenation (Pt catalyst at 310°). R. T.

Influence of cyclohexene concentration in the alkylation of benzene by cyclohexene. Dealkylation of cyclohexylbenzenes. B. B. CORSON and V. N. IPATIEV (J. Amer. Chem. Soc., 1937, 59, 645—647).—The degree of alkylation of C_6H_6 by cyclohexene (I) depends on the proportions used. AlCl_3 (60 g.), C_6H_6 (2.3), and (I) (3 mols.) at 3—18° give cyclohexyl- (II) (58 g.), b.p. 238.6—238.8°/756 mm., m.p. 6.6—7°, 1:4-dicyclohexyl- (III) (31 g.), b.p. 335—340°/756 mm., 1:3:5-tri- (IV) (158 g.), m.p. 68.5—69°, and 1:2:3:5-tetra-cyclohexyl-benzene (V) (1 g.), m.p. 264—265°. 2 mols. of C_6H_6 , 4 mols. of (I), and 60 g. of AlCl_3 in cyclohexane (150 g.) give 80 g. of (V). With H_2SO_4 (II), (III), and (V) are obtained. Further reaction of (II) and (III) readily gives (V), but (IV) gives mostly oils. Dealkylation (AlCl_3 in C_6H_6) of (III) and (IV) gives (II), that of (V) gives (II) and (IV), a small amount of a substance, $\text{C}_{18}\text{H}_{20}$, m.p. 168—169°, being also obtained in all cases. The structure of (II) follows from its conversion by Br into Ph_2 , that of (III) by dehydrogenation and hydrogenation (Ni; 220°/100 kg.) to dicyclohexylcyclohexane (VI), forms, m.p. 159.5—161° and 54—56°, that of (IV) by conversion by Br into 1:3:5- $\text{C}_6\text{H}_3\text{Ph}_3$ and by hydrogenation (Ni; 240°/120 kg.) to 1:3:5-tricyclohexylcyclohexane (VII), m.p. 158—159°, and that of (V) by its dealkylation and by hydrogenation to give (VI) and (VII). R. S. C.

Formation of benzene in the radiochemical polymerisation of acetylene. W. MUND and C. ROSENBLUM (J. Physical Chem., 1937, 41, 469—475).— C_2H_2 under the influence of α - and β -rays from Rn simultaneously polymerises into C_6H_6 and cuprene. C. R. H.

Benzenesulphonates of copper.—See A., I, 307.

Electrolytic hydrogenation of bromobenzene. M. BUSCH and W. WEBER (Ber., 1937, 70, [B], 744—746).—Electrolysis of alkaline-alcoholic solutions of PhBr at a Pd, Cu, Pb, or Hg cathode causes quant. removal of halogen at a rate which \propto the overvoltage of the cathode. C_6H_6 unmixed with Ph₂ is produced. H. W.

Catalytic dehydrogenation of ethylbenzene to styrene. J. S. SALKIND and G. L. BULAVSKI (Plast. Massui, 1935, No. 3, 9—12).—Passage of PhEt in N_2 over $\text{ZnO-Al}_2\text{O}_3$ (1:9) at 660—670°/10—13 mm. at the rate of 1 g. per min. yields 83% of styrene.

CH. ABS. (r)

$\alpha\alpha\mu\mu$ -Tetraphenyldodecahexaene. G. WITTIG and R. WIETBROCK (Annalen, 1937, 529, 162—166).— $\Delta^{8,8}$ -Hexadiene- $\alpha\alpha$ -dicarboxylic acid, PbO , and $\text{CPh}_2\text{:CH:CHO}$ in Ac_2O at 150° (CO_2) give orange-red $\alpha\alpha\mu\mu$ -tetraphenyldodecahexaene, m.p. 213—214.5°

[*octabromide*, m.p. 205—206° (decomp.)], which is reduced (PtO₂) to $\alpha\mu\mu$ -*tetraphenyldodecane*, m.p. 74—75°, and is not readily oxidised. The hexaene is decolorised only after 9 hr. in boiling xylene; $\alpha\omega\omega$ -*tetraphenyl-decapentaene* and -*octatetraene* require boiling for 16 and 25 hr., respectively. Polyenes of this series absorb $n - 2$ mols. of Br, n being the no. of CH:CH. R. S. C.

Dipole measurements on isomeric plato-complexes. III.—See A., I, 322.

Synthesis of 8 : 8'-dinitro-1 : 1'-dinaphthyl and related compounds. H. H. HODGSON and J. H. CROOK (J.C.S., 1937, 571—573).—8 : 1-NO₂·C₁₀H₇·NH₂ (I) in AcOH diazotised (conc. H₂SO₄) and treated with KI affords 1-*iodo-8-nitronaphthalene* (II), m.p. 80°, nitrated to 1-*iodo-4 : 8-dinitronaphthalene* (III), m.p. 146°, also produced by the Sandmeyer reaction on 4 : 8 : 1-(NO₂)₂C₁₀H₅·NH₂ (IV). (I) diazotised and treated with CuOH affords 8 : 8'-*dinitro-1 : 1'-dinaphthyl*, m.p. 295°, also obtained from (II) with Cu in boiling PhNO₂. (III) with Cu-PhNO₂ yields 4 : 8 : 4' : 8'-*tetranitro-1 : 1'-dinaphthyl*, m.p. 260°. Similarly, diazotised 8 : 4 : 1-NO₂·C₁₀H₅·Br·NH₂ with CuOH yields 4 : 4'-*dibromo-8 : 8'-dinitro-1 : 1'-dinaphthyl*, m.p. 294° (decomp.), also obtained from 4 : 1 : 8-C₁₀H₅·Br·I·NO₂ and Cu in boiling PhNO₂. (IV) diazotised and treated with CuOH yields 4 : 8 : 4' : 8'-*tetranitro-1 : 1'-dinaphthylamine*, m.p. 244°. J. D. R.

Dissociable anthracene oxides : photo-oxides of *meso*-ditolylanthracenes. A. WILLEMART (Bull. Soc. chim., 1937, [v], 4, 510—517).—Anthraquinone with *p*- or *m*-C₆H₄Me·MgBr gives 9 : 10-*dihydroxy-9 : 10-di-p*-, m.p. about 270° (block), and -*m-tolylanthracene*, m.p. 247—248° (block), reduced by KI-NaH₂PO₂-AcOH to 9 : 10-*di-p*-, m.p. 279°, and -*m-tolylanthracene*, m.p. 222° (block), which in light in CS₂ absorb 20 to give *photo-oxides*, which dissociate quantitatively when isolated. 9 : 10-*Di-otolylanthracene*, m.p. 347—348° (block), obtained from the 9 : 10-*diol*, m.p. 307—308° (block), absorbs O₂ much more slowly, but the product is also a dissociable photo-oxide. R. S. C.

Acenaphthene compounds.—See A., I, 307.

Action of sodamide and alkyl halides on *N*-arylformiminoethers. M. GRUNFELD (Bull. Soc. chim., 1937, [v], 4, 654—664).—Alkyl halides and the Na compounds formed from OEt·CH·NAr and NaNH₂ in C₆H₆ or PhMe give a mixture of equal proportions of HCO·NRAr and NAr·CH·NRAr together with some NHRAr and resinous products. Thus from OEt·CH·NPh and Bu⁺Br are obtained *form-n-butylanilide*, b.p. 155—157°/18 mm. [synthesised from HCO·NHPH-NaNH₂-Bu⁺Br; hydrolysed to give NHPH·Bu⁺ (NN'-*diphenyl-N'-n-butylcarbamide*, m.p. 68°)], and NN'-*diphenyl-N'-n-butylformamidine*, b.p. 189.5°/4 mm. (synthesised from NPh·CH·NHPH-NaNH₂-Bu⁺Br), recognised by its hydrolysis products NH₂Ph and NHPH·Bu⁺. Similarly using CH₂PhCl are obtained HCO·NPh·CH₂Ph and NN'-*diphenyl-N'-benzylformamidine*, b.p. 213—214°/2 mm. From *m*-C₆H₄Me·N·CH·OEt are obtained *N-m-tolyl-N-benzylformamidine*, m.p. 60—61° [hydrolysed to give

L (A., II.)

m-tolylbenzylamine (*hydrochloride*, m.p. 160—170°; Bz derivative, m.p. 69°)], and NN'-*di-m-tolyl-N'-benzylformamidine*, b.p. 224°/3 mm. [*hydrochloride*, m.p. 149—151°; *platinichloride*, m.p. 212—214° (decomp.)]. The NH₃ liberated in these reactions is < the theoretical quantity required for various suggested mechanisms. J. W. B.

Dissociation constants and rotations of some α -substituted ethylamines. J. M. BURCH (Iowa State Coll. J. Sci., 1935, 10, 55—57).—*sec*·NH₂Bu, α -benzyl-, α -*p*-tolyl-, α -phenyl-, α -*p*-diphenyl-, and α -*o*-chlorobenzyl-ethylamine were resolved and the rotations of the pure amines, of their MeOH, EtOH, and C₆H₁₄ solutions, and of the MeOH solutions of their hydrochlorides measured. The rotations of the α -substituted ethylamines were correlated with dissociation const. vals., with dipole moments, and with the nature of the substituent. CH. ABS. (e)

Preparation of diphenyl-*p*-tolylamine and phenyldi-*p*-tolylamine. R. J. B. MARSDEN (J.C.S., 1937, 627).—NHPH₂ and NH(C₆H₄Me)₂ with *p*-C₆H₄MeI·K₂CO₃-Cu-bronze in boiling PhNO₂ afford, respectively, *diphenyl-p-tolylamine*, b.p. 230—244°/40 mm., m.p. 68.75° (corr.), and *phenyldi-p-tolylamine*, m.p. 109° (corr.). J. W. B.

Velocity of acetylation of aromatic aminosulphonic acids. A. I. TITOV and A. N. BARSCHNIKOVA (J. Gen. Chem. Russ., 1937, 7, 357—362).—The velocity of acetylation of 1 : 6- and 1 : 7-NH₂·C₁₀H₆·SO₃H has been determined under different conditions. R. T.

Manufacture of acylated aromatic amines containing the trichloromethyl group.—See B., 1937, 327.

Manufacture of aromatic amines containing the trifluoromethyl group.—See B., 1937, 327.

Formation and decomposition of quaternary ammonium salts in solution.—See A., I, 313.

1 : 3-Diamino-1 : 2 : 2-trimethylcyclopentane. J. SUSZKO and F. TRZEBNIAK (Rocz. Chem., 1937, 17, 105—110).—1 : 3-Diamino-1 : 2 : 2-trimethylcyclopentane, m.p. 141° (lit. 124°) (*carbonate*, +H₂O, m.p. 124°; *diurethane*, m.p. 173°), is prepared by hydrolysis of the corresponding 1 : 3-diazide, prepared from camphoric acid. R. T.

Complex salts of the racemic and optically active diaminocyclohexanes with tervalent cobalt and rhodium. III. Tridiaminocyclohexane salts of tervalent cobalt. F. M. JAEGER and L. BIJKERK (Proc. K. Akad. Wetensch. Amsterdam, 1937, 40, 246—258; cf. A., I, 170).—When CoCl₂·6H₂O (30 g.) dissolved in H₂O (110 c.c.) is mixed with *r*-, *d*-, or *l*-diaminocyclohexane (Chxn) (27.5 g.) at 15° and 10% H₂O₂ (240 c.c.) is added slowly and with continuous shaking, a reddish-brown solution is obtained, which, after heating to remove excess of H₂O₂, addition of conc. HCl (450 c.c.), evaporation to dryness, and extraction with EtOH, yields a dark green hygroscopic mass of the compound [Co(Chxn)₂Cl₂]Cl (I). On refluxing the *r*-form of (I) with theoretical amount of *r*-diaminocyclohexane for 3 hr. the compound [Co(*r*-Chxn)₃]Cl₃·H₂O (II)

is formed. The compounds $[\text{Co}(\text{r-Chxn})_3](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (III), $[\text{Co}(\text{r-Chxn})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ (IV), $[\text{Co}(\text{r-Chxn})_3](\text{ClO}_3)_3$ (V), and $[\text{Co}(\text{r-Chxn})_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ (VI) are also described. (II) can be resolved through the chloro-*d*-tartrates, the least sol. being the compound *L*- $[\text{Co}(\text{d-Chxn})_3]\text{Cl}(\text{C}_4\text{H}_4\text{O}_6) \cdot 2\text{H}_2\text{O}$, and the most sol. the compound *D*- $[\text{Co}(\text{l-Chxn})_3]\text{Cl}(\text{C}_4\text{H}_4\text{O}_6) \cdot 5\text{H}_2\text{O}$ (VIII). The crystal structures of (II)—(VIII) are described and the rotatory dispersion of (VII) and (VIII) have been investigated. J. W. S.

Constitution of compounds of cyclic diamines with metallic salts. R. CERNATESCU, (MME.) M. PAPAFIL, and (MLLE.) M. PONI (Ann. Sci. Univ. Jassy, 1935, 20, 175—189).—By determination of the wt. of (1) NH_3 fixed and (2) base (*B*) displaced when dry NH_3 is passed over the compounds of various metallic salts with diamines it is found whether each mol. of *B* is replaced by 1 mol. of NH_3 (*B* united by one valency) or by 2 (*B* united by two valencies). Thus 1 : 8- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ is united by one valency in $\text{CdCl}_2 \cdot 2\text{B}$ and $\text{CdBr}_2 \cdot 2\text{B}$, but by two valencies in $\text{NiSO}_4 \cdot 2\text{B}$; in $\text{CdBr}_2 \cdot \text{B}$, *B* is united by one valency when it is 1 : 2, and by two valencies when it is 1 : 5- $\text{C}_{10}\text{H}_8(\text{NH}_2)_2$. With *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ the base is united by two valencies in $\text{CdCl}_2 \cdot \text{B}$, $\text{CdI}_2 \cdot \text{B}$ (I), $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{B}$, and $\text{NiCl}_2 \cdot 2\text{B}$, and also in $\text{CdBr}_2 \cdot \text{p-C}_6\text{H}_4\text{Me}(\text{NH}_2)_2$. Contrary to Hieber *et al.* (A., 1931, 412), ebullioscopic determination in $\text{C}_5\text{H}_5\text{N}$ shows that (I) is a simple mol. and must, therefore, have the structure $\text{C}_6\text{H}_4(\text{NH}_2 \dots)_2\text{MX}_2$. J. W. B.

2 : 3-Diaminonaphthalene. H. GOLDSTEIN and M. STREULI (Helv. Chim. Acta, 1937, 20, 520—524).—2 : 3- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ (I) is conveniently obtained by heating 2 : 3-OH- $\text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ with $(\text{NH}_4)_2\text{SO}_3 \cdot \text{NH}_3$ at 170° in an enamelled autoclave. It gives a picrate, m.p. 210° (corr.), and a *Bz*₂ derivative, m.p. 271° (corr.). When heated with 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ and cryst. NaOAc in EtOH (I) gives 3-amino-2 : 2' : 4'-dinitroanilinonaphthalene, m.p. 200° (corr.). (I), NaOAc , and picryl chloride in EtOH at 60° give 3-amino-2 : 2' : 4' : 6'-trinitroanilinonaphthalene, m.p. 202° (corr.; decomp.), which is not cyclised when heated with C_{10}H_8 at 200—205°. With 2 : 4-dinitronaphthyl *p*-toluenesulphonate in EtOH at 100° (I) affords 3-amino-2 : 2' : 4'-dinitro-1'-naphthylaminonaphthalene, m.p. 213° (corr.; decomp.), which does not lose HNO_2 in boiling C_{10}H_8 or quinoline. (I) is converted by boiling HCO_2H into lin.-naphthiminazole, m.p. 218° (corr.), and by boiling AcOH into 2-methylin.-naphthiminazole, m.p. 285° (corr.). (I), PhN_2Cl and NaOAc afford 2 : 3-diamino-1 : 4-dibenzeneazonnaphthalene, from which 1 : 2 : 3 : 4- $\text{C}_{10}\text{H}_4(\text{NH}_2)_4$ could not be obtained. H. W.

Regularities of colour indicators. H. EICHLER (Monatsh., 1937, 70, 79—83).—The groups responsible for the indicator colour changes in *p*- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{NPh}$ and in *p*-OH- $\text{C}_6\text{H}_4 \cdot \text{N} : \text{NPh}$ show their characteristic colour changes at the same p_K vals. in 4-amino-4'-hydroxyazobenzene (hydrochloride; nitrate) which is red in acid and yellow in alkaline solution. At p_K where no salt formation occurs either with NH_2 or OH the pale yellow neutral compound tends to be pptd. J. W. B.

Action of hydrazine and methylhydrazine on 1 : 5-dichloro-2 : 4-dinitrobenzene and derivatives of the compounds obtained. (Miss) J. L. ROBERT (Rec. trav. chim., 1937, 56, 413—436).—5-Chloro-2 : 4-dinitrophenylhydrazine (A., 1921, i, 461) with boiling aq. EtOH containing CuSO_4 affords 1 : 2 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ and with aldehydes and ketones in boiling EtOH containing H_2SO_4 affords the corresponding hydrazones. 5-Chloro-2 : 4-dinitrophenylhydrazones [m.p. (block) in parentheses] of the following aldehydes and ketones are prepared: MeCHO (192°); COEt₂ (108°); Me hexyl ketone (76°); heptaldehyde (108°); COPhMe (213°); *o*- (193° and 213°), *m*- (286°), and *p*- $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CHO}$ (282°); *o*- (231° and 237°), *m*- (263°), and *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ (335°); *p*-OH- $\text{C}_6\text{H}_4 \cdot \text{CHO}$ (275° and 281°); *p*-OMe- $\text{C}_6\text{H}_4 \cdot \text{CHO}$ (237°); *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{CHO}$ (227° and 247°); *p*- $\text{C}_6\text{H}_4\text{Pr}^{\beta} \cdot \text{CHO}$ (213° and 225°); *o*-OH- $\text{C}_6\text{H}_4 \cdot \text{CHO}$ (290°); 4-hydroxy-3-methoxybenzaldehyde (266°); 3 : 4-methylenedioxybenzaldehyde (247°); furfuraldehyde (234°); 5-methyl- (202°) and 5-hydroxymethyl-furfuraldehyde (208°). $\text{NHMe} \cdot \text{NH}_2$ with 1 : 5-dichloro-2 : 4-dinitrobenzene (I) in boiling EtOH affords 5-chloro-2 : 4-dinitrophenylmethylhydrazine (II), m.p. 183° (block) [Ac derivative, m.p. 186° (block) and 197° after resolidifying], which with CuSO_4 in boiling aq. EtOH gives 5-chloro-2 : 4-dinitromethylaniline, m.p. 161—163° (lit., 106—107°). 5-Chloro-2 : 4-dinitrophenylmethylhydrazones [m.p. (block) in parentheses] of the following aldehydes and ketones are described: CH_2O (152°); MeCHO (200°); COMe₂ (192°); COEt₂ (90°); Me hexyl ketone (55—58°); $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$ [127° (Thiele)]; heptaldehyde (45—46°); COPhMe [143° (Thiele)]; PhCHO (197°); *o*- (176°), *m*- (196°), and *p*- $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CHO}$ (206° and 219°); *o*- (222°), *m*- (239°), and *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ (279°); *p*-OH- $\text{C}_6\text{H}_4 \cdot \text{CHO}$ (197°, 205°, and 215°); *o*-OH- $\text{C}_6\text{H}_4 \cdot \text{CHO}$ (237°); *p*-OMe- $\text{C}_6\text{H}_4 \cdot \text{CHO}$ (227°); *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{CHO}$ (219°); *p*- $\text{C}_6\text{H}_4\text{Pr}^{\beta} \cdot \text{CHO}$ (154° and 163°); 4-hydroxy-3-methoxy- (217°) and 3 : 4-methylenedioxy-benzaldehyde (214°); furfuraldehyde (205°); 5-methyl- (132° and 173°) and 5-hydroxymethyl-furfuraldehyde (108°). $\text{NHMe} \cdot \text{NH}_2$ with (I) in boiling EtOH affords (II) and 2 : 4-dinitro-1 : 5-di-(α -methylhydrazino)benzene (III), m.p. 270° (block) [Ac derivative, m.p. 350° (block)] (cf. *loc. cit.*), which with FeCl_3 in boiling EtOH affords 2 : 4-dinitrophenylene-1 : 3-dimethylamine (cf. A., 1902, i, 715). (III) reacts as above with the following ketones and aldehydes to give 2 : 4-dinitrophenylene-1 : 5-di- α -methylhydrazones [m.p. (block) in parentheses]: CH_2O (150° and 163°); COPhMe (206°); PhCHO (236°); *o*-OH- $\text{C}_6\text{H}_4 \cdot \text{CHO}$ (245°); furfuraldehyde (106°, 203°, and 213°); and 4 : 6-dinitro-1 : 3-di-(α -methyl- β -acetylhydrazino)benzene (305°). Similarly, 2 : 4-dinitrophenylene-1 : 5-di-hydrazones of the following are prepared: COPhMe (270°); *o*-OH- $\text{C}_6\text{H}_4 \cdot \text{CHO}$ (324°); and furfuraldehyde (293°). (II) with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in boiling EtOH affords 2 : 4-dinitro-1-hydrazino-5-(α -methylhydrazino)benzene, m.p. 193—194° (block) [Ac₂ derivative (IV), m.p. 268° and 283° (block)] (obtained in 4 cryst. forms), which gives with CuSO_4 , FeCl_3 , and HgO unidentified oxidation products and reacts with the following aldehydes and ketones to give dihydrazones [m.p.

(block) in parentheses]: CH_2O (190°); MeCHO (178°); COMe_2 (147°); COEt_2 [110—112° (Thiele)]; Me hexyl ketone (86°); heptaldehyde (95°); COPhMe (201°); PhCHO (243°); *o*-(236°), *m*-(206° and 231°), and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ (271°); *o*-(246° and 256°), *m*-(280°), and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (325°); *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (205° and 290°); *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (281°); *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (248°); *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ (222° and 248°); *p*- $\text{C}_6\text{H}_4\text{Pr}^n\cdot\text{CHO}$ (241° and 354°); vanillin (201° and 242°); piperonaldehyde (200° and 267°); furfuraldehyde (256°); 5-methyl- (190° and 223°) and 5-hydroxymethyl-furfuraldehyde (decomp. 223°; (IV) (268° and 283°); and the 2:4-dinitro-5-(α -methylhydrazino)phenylhydrazine [172° (V)] of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$. 5-Chloro-2:4-dinitrophenylhydrazine with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in boiling EtOH containing H_2SO_4 affords the 5-chloro-2:4-dinitrophenylhydrazine of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, which with the calc. amount of $\text{NHMe}\cdot\text{NH}_2$ in boiling EtOH affords (V). J. L. D.

Connexion between complex formation and redox reactions. I. L. KULBERG (J. Gen. Chem. Russ., 1937, 7, 381—387).—Oxidation of org. compounds by Ag^+ depends not only on the E_0 of the compound, but also on whether complex formation with Ag^+ takes place. This is shown to be the case for a series of phenols, aminophenols, and CHPh_3 dyes. R. T.

Effect of substituents on the germicidal activity of phenols. I. Alkyl derivatives of 2:4-dibromophenol. S. L. CHIEN, H. P. CHUNG, and H. C. TAI (J. Chinese Chem. Soc., 1936, 4, 361—369).—2:4- $\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH}$ and 3:5-dibromo-*o*-cresol are prepared in 86 and 95% yield, respectively. The following are obtained by acylation of the phenol, Fries rearrangement, and Clemmensen reduction. 2:4-Dibromophenyl acetate, m.p. 36°, propionate, b.p. 145—146°/15 mm., butyrate, b.p. 178—181°/20 mm., and valerate, b.p. 153—154°/1 mm. 3:5-Dibromo-2-hydroxy-aceto-, m.p. 109—110°, propio-, m.p. 116.5—117°, butyro-, m.p. 71—72°, and valerophenone, m.p. 74.5—76°. 2:4-Dibromo-6-ethyl-, b.p. 121—122°/3.5 mm., *n*-propyl-, b.p. 130—131°/4.5 mm., *n*-butyl-, b.p. 139—141°/2 mm., and *n*-amylphenol, b.p. 159—161°/4 mm. R. S. C.

New aromatic fluoro-derivatives. A. C. DE DEGIORGI and E. V. ZAPPI (Anal. Assoc. Quim. Argentina, 1936, 24, 119—130).—3-Fluoro-5-nitroanisole (I) (A., 1936, 1374) with Sn and HCl gives 3-fluoro-5-aminoanisole, a liquid (sulphate; dihydrate) which on diazotisation and decomp. in presence of NaNO_2 gives (I), and with HCl for 5 hr. at 170—180° yields 3-fluoro-5-nitrophenol (II), m.p. 112°, which on methylation gives (I). Diazotised 3-nitro-5-amino-phenetole with 40% HBF_4 gives 3-nitrophenetole-5-diazonium borofluoride, decomp. 110°, which loses BF_3 at 110° to yield 3-fluoro-5-nitrophenetole, m.p. 63.5—64°, hydrolysed to (II). 1:3:5- $\text{C}_6\text{H}_3\text{F}(\text{NO}_2)_2$ with 1 mol. of $(\text{NH}_4)_2\text{S}$ in aq. EtOH yields 3-fluoro-5-nitroaniline, m.p. 115—116°, which by diazotisation and subsequent decomp. yields *m*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NO}_2$. F. R. G.

Cleavage of diphenyl ethers by sodium in liquid ammonia. I. *o*- and *p*-Substituted di-

phenyl ethers. P. A. SARTORETTO and F. J. SOWA (J. Amer. Chem. Soc., 1937, 59, 603—606).—By determination of the cleavage products produced from substituted Ph_2 ethers by Na in liquid NH_3 the following are found to increase the strength of the $\text{Ph}\cdot\text{O}$ linking: *o*- < *p*- Me < *p*- OMe < *o*- < *p*- NH_2 , whilst the following decrease it: *o*- OMe < *o*- < *p*- CO_2Na . Thus, the tautomeric effect dominates the inductive effect, except for *o*- OMe . *Ph p*-, b.p. 200°/15 mm., m.p. 56—58°, and *o*-nitro-, b.p. 185°/8 mm., *p*-, b.p. 188°/14 mm., m.p. 83.5°, and *o*-amino-, b.p. 170°/18 mm., m.p. 44°, *o*-, m.p. 112—114°, and *p*-carboxy-phenyl ether, m.p. 141°, *Ph o*-, b.p. 191°/5 mm., and *p*-tolyl, b.p. 114°/6 mm., *o*-, b.p. 288°/745 mm., m.p. 76°, and *p*-anisyl ether, b.p. 125°/5 mm., *o*-tolyl *p*-tolyl ether, b.p. 121°/7 mm., and *o*-anisyl *p*-anisyl ether, b.p. 203°/20 mm., m.p. 77°, are described. R. S. C.

Iodination of phenols. C. V. BORDEIANU (Ann. Sci. Univ. Jassy, 1935, 20, 131—138).—Iodination of phenols is readily effected (a) with $\text{I}\cdot\text{MeOH}$ and the phenol in $\text{MeOH}\cdot\text{NH}_3$, or (b) by addition of $\cdot\text{HgAc}$ derivatives in alkaline solution to $\text{I}\cdot\text{AcOH}$. Thus are prepared (a) iodo-*o*-xlenol and the I_2 -derivative, m.p. 176—177° (decomp.) (*Ac* derivative, m.p. 153—154°), of *m*-5-xlenol, and (b) 2:6-di-iodo-3-hydroxy-*p*-xylene, m.p. 63°. 6-Bromo-2-iodothymol was obtained by method (b). J. W. B.

Colour of 2-nitrodiphenylamine-4-arsinic acid derivatives, containing additional auxo-groups.

II. Colour of nitrobenzoyl derivatives of aromatic amines. III. Influence of position of nitro-

and auxo-groups on colour of nitrobenzoylarylamines. V. A. ISMAILSKI and E. A. SMIRNOV

(J. Gen. Chem. Russ., 1937, 7, 513—522, 523—537; cf. this vol., 267).—II. The $\text{CO}\cdot\text{NH}$ group is shown to act as a chromophore in a no. of *m*- and *p*-nitrobenzoyl derivatives of substituted anilines, the intensity of coloration depending on the nature and position of the auxochrome groups. The *N*-*p*-nitrobenzoyl derivatives of *m*-aminophenol, m.p. 212°, *p*-anisidine, m.p. 197°, *m*-, m.p. 188°, and *p*-dimethylaminoaniline, m.p. 258.5°, and the *m*-nitrobenzoyl derivatives of *m*-aminophenol, m.p. 219°, *p*-anisidine, m.p. 174.5°, *p*-*N*-methylaminophenol, m.p. 224°, *m*-, m.p. 176°, and *p*-dimethylaminoaniline, m.p. 173°, are described.

III. The absorption spectra of the above compounds are given, and the causes of differences in absorption for *m*- and *p*-substituted compounds are discussed. R. T.

Derivatives of 3-amino-2-naphthol. H. GOLDSTEIN and P. GARDIOL [with M. COMTESSE, R. MOHR, and H. FISCHER] (Helv. Chim. Acta, 1937, 20, 516—520).—2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ (I) gives a *picrate*, m.p. 206° (decomp.). (I) is transformed by boiling 90% HCO_2H into 3-formamido-2-naphthol, m.p. 193° (corr.), and by cold Ac_2O into 3-acetamido-2-naphthol, m.p. 244° (corr.). 2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHBz}$ is converted by BzCl and NaOH at 100° into its *benzoate*, m.p. 184° (corr.), and by boiling Ac_2O into the corresponding *acetate*, m.p. 154° (corr.). (I) yields a very unstable diazo-compound from which 3:2- $\text{C}_{10}\text{H}_6\cdot\text{I}\cdot\text{OH}$, m.p. 105° (corr.), is obtained in poor yield. (I) couples with *p*- $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ in alkaline solution and the

resulting compound is reduced by SnCl_2 and HCl to 1:3-diamino-2-naphthol [dihydrochloride; Ac_3 derivative, m.p. 239° (corr.)]. Similar coupling in acid solution followed by reduction leads to 3:4-diamino-2-naphthol dihydrochloride. (I) is converted by PhI , K_2CO_3 , and Cu powder in boiling PhMe into 2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHPh}$, m.p. 131° (corr.). H. W.

Syntheses in the phenanthrene series. VI. 3-Methoxy-1-methylphenanthrene. P. HILL, W. F. SHORT, H. STROMBERG, and A. E. WILES (J.C.S., 1937, 510—513).—The Mg compound (I) of 6-bromo-*m*-tolyl Me ether with β -chloroethyl *p*-toluenesulphonate in C_6H_6 gives β -(5-methoxy-*o*-tolyl)ethyl chloride, b.p. $134\text{—}135^\circ/10\text{ mm.}$, the Mg compound of which with cyclohexanone gives $\alpha\delta$ -di-(5-methoxy-*o*-tolyl)-butane, m.p. 87° , and the crude cyclohexanol, dehydrated by KHSO_4 at 165° to 1- β -(5'-methoxy-*o*-tolyl)-ethyl- Δ^1 -cyclohexene, b.p. $192\text{—}195^\circ/18\text{ mm.}$ This with AlCl_3 in CS_2 at 0° —room temp. and dehydrogenation of the product with S at $180\text{—}240^\circ$ gives 3-methoxy-1-methylphenanthrene (II), m.p. 90° [picrate (III), m.p. 147°]. (I) and $\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{Br}$ give 6-allyl-*m*-tolyl Me ether, b.p. $107\text{—}108^\circ/10\text{ mm.}$, oxidised by 5% KMnO_4 -aq. AcOH at $<0^\circ$ to 5-methoxy-*o*-tolylacetic acid, m.p. $106.5\text{—}107^\circ$, the K salt of which with *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in Ac_2O at 100° gives 2-nitro-, m.p. $169.5\text{—}170^\circ$, reduced by FeSO_4 -aq. NH_3 to the (unstable) 2-amino- α -(5'-methoxy-*o*-tolyl)-cinnamic acid, m.p. $171\text{—}172^\circ$, diazotisation of which affords 3-methoxy-1-methylphenanthrene-10-carboxylic acid, m.p. $199\text{—}200^\circ$, decarboxylated by Cu powder in quinoline at 230° to (II). Demethylation of (II) with HI (*d* 1.7)— AcOH affords 3-hydroxy-1-methylphenanthrene (IV), m.p. 161° . This couples with diazotised *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ to give a red dye, reductive fission of which with $\text{Na}_2\text{S}_2\text{O}_4$ gives an unstable NH_2 -phenol, oxidised by CrO_3 - AcOH at 0° to 1-methylphenanthra-3:4-quinone, decomp. 300° , converted by $\text{Zn}\text{—}\text{Ac}_2\text{O}\text{—}\text{C}_5\text{H}_5\text{N}$ into 3:4-diacetoxy-1-methylphenanthrene, m.p. $138.5\text{—}139^\circ$. The m.p. of (II), (III), and (IV) are depressed by admixture with the isomeric compounds obtained by dehydrogenation of podocarpic acid. J. W. B.

Synthesis of halogenated thiocresols. S. L. CHIEN and H. T. KUAN (J. Chinese Chem. Soc., 1936, 4, 355—360).—*o*-Toluidine-5-sulphonic acid affords (diazo-reaction) 2-bromotoluene-5-sulphonic acid, the chloride of which with $\text{Sn}\text{—}\text{HCl}$ gives 6-bromo-*m*-thiocresol, m.p. $80\text{—}81^\circ$ (lit. an oil). Similarly are prepared 4-bromo-*o*-, b.p. $107\text{—}108^\circ/2\text{ mm.}$, 4-chloro-*o*-, m.p. $80\text{—}81^\circ$, and *m*-thiocresol, m.p. $67\text{—}68^\circ$, and 4-chlorotoluene-2-, m.p. 24° , and -3-sulphonyl chloride, m.p. 50° . R. S. C.

Reaction between thallium chloride and bromide and certain phenols. N. N. MELNIKOV and G. P. GRATSHEVA (J. Gen. Chem. Russ., 1937, 7, 467—469).— TiCl_3 or TlBr_3 and α - or β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ in H_2O yield thallium tri- α -, m.p. $74\text{—}78^\circ$, and tri- β -naphthoxide, m.p. $109\text{—}112^\circ$. *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ are oxidised by TiCl_3 , with production of quinones and TiCl . Phloroglucinol yields a highly toxic additive compound, $\text{C}_6\text{H}_3(\text{OH})_3\cdot\text{TlBr}_3$, decomp. at 200° . R. T.

Pharmacologically active compounds from β -alkoxyphenylethylamines. W. S. IDE and J. S. BUCK (J. Amer. Chem. Soc., 1937, 59, 726—731).—The following are prepared by methods previously described, starting from the appropriate phenolic aldehydes. 3:4-Diethoxycinnamic acid, m.p. 156° . γ -3-Methoxy-2-ethoxyphenylpropionic acid, m.p. 65° (amide, m.p. 85°). γ -*o*-, m.p. 106° , -*m*-, m.p. 80° , and -*p*-Ethoxyphenylpropionamide, m.p. 137° . β -*o*-, b.p. $128\text{—}130^\circ/13\text{ mm.}$ (hydrochloride, m.p. 218° ; *p*-nitrobenzoyl derivative, m.p. 120°), -*m*-, b.p. $135\text{—}138^\circ/13\text{ mm.}$ (hydrochloride, m.p. 168° , gels at 146° ; *p*-nitrobenzoyl derivative, m.p. 113°), and -*p*-ethoxy-, b.p. $138\text{—}140^\circ/3\text{ mm.}$ (hydrochloride, m.p. 206° ; *p*-nitrobenzoyl derivative, m.p. 154°), -3-methoxy-2-ethoxy-, b.p. $148\text{—}150^\circ/13\text{ mm.}$ (hydrochloride, m.p. 162° ; *p*-nitrobenzoyl derivative, m.p. 102°), -3-methoxy-4-ethoxy-, b.p. $160^\circ/13\text{ mm.}$ (hydrochloride, m.p. 168° ; *p*-nitrobenzoyl derivative, m.p. 157°), -4-methoxy-3-ethoxy-, b.p. $168^\circ/15\text{ mm.}$ (hydrochloride, m.p. 168° ; *p*-nitrobenzoyl derivative, m.p. 156°), and -3:4-diethoxy-phenylethylamine, b.p. $158^\circ/13\text{ mm.}$ [hydrochloride, new m.p. 198° (gels at 144°); *p*-nitrobenzoyl derivative, m.p. 138°]; the corresponding β -phenylethylmethylamines, b.p. $97^\circ/2\text{ mm.}$, $106^\circ/2\text{ mm.}$, $107^\circ/2\text{ mm.}$, $119^\circ/1.5\text{ mm.}$, $128^\circ/1.5\text{ mm.}$, $129^\circ/1.5\text{ mm.}$, and $129^\circ/2\text{ mm.}$ (hydriodides, m.p. 118° , 74° , 129° , 122° , 228° , 154° , and 100° , respectively; hydrochlorides, m.p. 133° , 144° , 206° , 147° , 131° , 159° , and 157° ; *p*-nitrobenzoyl derivatives, m.p. 235° , 222° , 118° , 78° , 155° , 102° , and 58° , respectively); the corresponding phenylethylcarbamides, m.p. 112° , 104° , 134° , 120° , 126° , 145° , and 108° , respectively; the corresponding *as*-methylcarbamides, m.p. 84° , 118° , 149° , 76° , 112° , 96° , and 97° , respectively; the corresponding 1- β -*x*-alkoxyphenylethyl-5:5-diethylbarbituric acids, m.p. 66° , 86° , 134° , 68° , 120° , 99° , and 88° , respectively; the corresponding *N*-benzylamine hydrochlorides, m.p. 122° , 194° , 240° , 162° , 200° , 195° , and 190° , respectively; the corresponding *N*-*o*'-ethoxybenzylamine hydrochlorides, m.p. 153° , 135° , 143° , 168° , 128° , 174° , and 168° , respectively; the corresponding *N*-*m*'-ethoxybenzylamine hydrochlorides, m.p. 113° , 146° , 167° , 124° , 106° , 103° , and 104° , respectively; the corresponding *N*-*p*'-ethoxybenzylamine hydrochlorides, m.p. 134° , 195° , 280° , 120° , 239° , 218° , and 208° , respectively; the corresponding *N*-3':4'-diethoxybenzylamine hydrochlorides, m.p. 148° , 114° , 186° , 113° , 154° , 122° , and 112° , respectively. β -*o*-Ethoxyphenylethyl-*N*-*o*'-ethoxybenzylamine, m.p. 133° . β -3-Methoxy-4-ethoxy-, m.p. 78° , and -3:4-diethoxy-phenylethyl-*N*-*p*'-ethoxybenzylamine, m.p. 108° . β -3-Methoxy-4-ethoxy-, m.p. 92° , and -3:4-diethoxy-phenylethyl-*N*-3':4'-diethoxybenzylamine, m.p. 98° . *p*'-Ethoxy-, m.p. 90° , and 3':4'-diethoxybenzylidene- β -*p*-ethoxyphenylethylamine, m.p. 86° ; benzylidene-, m.p. 67° , *p*'-ethoxy-, m.p. 107° , and 3':4'-diethoxybenzylidene- β -3-methoxy-4-ethoxyphenylethylamine, m.p. 115° ; *o*'-, m.p. 66° , and *p*'-ethoxy-, m.p. 60° , and 3':4'-diethoxybenzylidene- β -4-methoxy-3-ethoxyphenylethylamine, m.p. 96° ; *o*'-, m.p. 52° , and *p*'-ethoxy-, m.p. 96° , and 3':4'-diethoxybenzylidene- β -3:4-diethoxyphenylethylamine, m.p. 122° . 6-Ethoxy-, m.p. 251° [*N*-*Me* derivative (hydrochloride, froths at 144° , decomp. 220°)], 6-

methoxy-5-ethoxy, m.p. 184° [N-Me derivative (*hydrochloride*, m.p. 220°)], *6-methoxy-7-ethoxy*, m.p. 284° [N-Me derivative (*hydrochloride*, m.p. 270°)], *7-methoxy-6-ethoxy*, m.p. 282° [N-Me derivative (*hydrochloride*, m.p. 208°)], and *6:7-diethoxy-1:2:3:4-tetrahydroisoquinoline hydrochloride*, m.p. 268° [N-Me derivative (*hydrochloride*, m.p. 198°)].

R. S. C.

Synthesis of long-chain substituted isocyclics and similarly substituted adipic acids. (A) Preparation of *4-tert.-octylcyclohexanol*, -*hexene*, -*hexanone*, -*hexyl-hydroxylamine*, -*amine*, and -*phenol*, and β -*tert.-octyladipic acid*. J. B. NIEDERL and R. A. SMITH. (B) Preparation of *2-tert.-octylcyclohexanone*. Method of indirect proof of structure for *o*- and *p*-alkylphenols. J. B. NIEDERL and J. B. WHITMAN (J. Amer. Chem. Soc., 1937, 59, 715—717, 717—718).—(A) *4- $\alpha\alpha\gamma\gamma$ -Tetramethylbutylcyclohexanol* (I) (prep. by hydrogenation of "*p*-diisobutylphenol"), b.p. 148—150°/11.5 mm., m.p. 55.5—56°, with a little H_2SO_4 at 130—140° gives *$\alpha\alpha\gamma\gamma$ -tetramethylbutyl- Δ^3 -cyclohexene* (II), b.p. 113°/12 mm., and with $\text{K}_2\text{Cr}_2\text{O}_7$ gives *4- $\alpha\alpha\gamma\gamma$ -tetramethylbutylcyclohexanone* (III), b.p. 142—144°/11 mm. (NaHSO_3 compound). (II), PhOH , and H_2SO_4 at 60° give *p-4'- $\alpha\alpha\gamma\gamma$ -tetramethylbutylcyclohexylphenol*, m.p. 81°, b.p. 110—120°/2 mm. The *oxime*, m.p. 152°, of (III) with H_2 -Ni in 95% EtOH at 3.3 atm. yields *4- $\alpha\alpha\gamma\gamma$ -tetramethylbutylcyclohexylhydroxylamine hydrochloride*, m.p. 240—245° (decomp.), and thence by Na-EtOH the *amine hydrochloride*, m.p. 260—265° (decomp.). (I), (II), or (III) with 50% HNO_3 and, best, a trace of V_2O_5 at 110° gives 60% of β -*4- $\alpha\alpha\gamma\gamma$ -tetramethylbutyladipic acid*, m.p. 133—134°.

(B) *o*- and *p*-Alkylphenols can be differentiated by reduction to the *cyclohexanol* and oxidation; the former give adipic acid, the latter a β -substituted adipic acid. For comparison the *o*-alkylphenol can be obtained from *cyclohexanone*, NaNH_2 , and the alkyl bromide. *2- $\alpha\alpha\gamma\gamma$ -Tetramethylbutylcyclohexanone*, b.p. 140—144°/11 mm. (*oxime*, m.p. 147—148°), is thus obtained in 16% yield and oxidised.

R. S. C.

Preparation of diastereoisomeric pairs of alcohols. P. JULLIEN and F. KAYSER (Bull. Soc. chim., 1937, [v], 4, 700—711).—Contrary to the behaviour of MgPhBr (A., 1936, 1375), MgEtBr , MgBu^nBr , and $\text{CH}_2\text{Ph-MgCl}$ react with aldehydes to give a mixture of the two diastereoisomerides. Thus CHPhEt-CHO and MgEtBr in dry Et_2O give a mixture of (α)-, m.p. 47.5° (*phenylurethane*, m.p. 109°) and (β)- *γ -phenylhexan-8-ol*, b.p. 119—121°/15 mm. (*phenylurethane*, m.p. 127°); with MgBu^nBr are obtained (α)-, m.p. 51°, and (β)- *γ -phenyl-n-octan-8-ol*, b.p. 148—151°/17 mm. (*phenylurethane*, m.p. 106°), and $\text{CH}_2\text{Ph-MgCl}$ affords a mixture of (α)-, m.p. 140° (*phenylurethane*, m.p. 65°), and (β)- *$\alpha\gamma$ -diphenyl-n-pentan-3-ol*, m.p. 77° (*phenylurethane*, m.p. 94°). From the products of the action of $\text{CH}_2\text{Ph-MgCl}$ with CHMePh-CHO only (β)- *$\alpha\gamma$ -diphenyl-n-butan-2-ol*, m.p. 76° (*phenylurethane*, m.p. 90—91.5°), is isolated. The β -forms of these alcohols are the sole products obtained by reduction of the corresponding ketones with Na-EtOH. The ketones were prepared by the

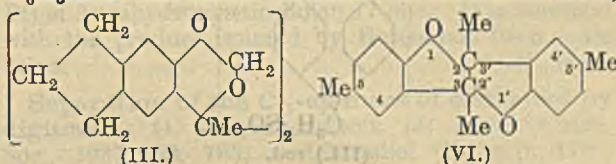
action of the appropriate MgRX on CHEtPh-CO-NH_2 or CHEtPh-CN and thus is obtained α -*phenyl-n-propyl Buⁿ ketone*, b.p. 133—134°/14 mm. (*semicarbazone*, m.p. 99°); prepared by various methods $\text{CHEtPh-CO-CH}_2\text{Ph}$ has b.p. 187—189°/17 mm. (*semicarbazone*, m.p. 143°).

J. W. B.

Molecular rearrangements during the dehydration of *4-methylcyclohexylisopropylpinacol*. M. GODCHOT and (Mlle.) G. CAUQUIL (Compt. rend., 1937, 204, 733—736).—Me *4-methylcyclohexan-1-ol-1-carboxylate* (this vol., 149) with MgMeI affords *1-(β -hydroxyisopropyl)-4-methylcyclohexanol*, m.p. 95—96°, dehydrated by aq. $\text{H}_2\text{C}_2\text{O}_4$ at 120° to a mixture of *1-methyl-4-isopropenyl- Δ^3 -cyclohexene* (60%) (Raman spectrum determined), *2:2:5-trimethylcycloheptanone* (4%), b.p. 86—87°/12 mm. (*semicarbazone*, m.p. 200—201°; *oxime*, m.p. 62°); and *1:4-dimethylcyclohexyl Me ketone* (36%), b.p. 85°/12 mm. (*semicarbazone*, m.p. 156°; *oxime*, m.p. 123°), oxidised by NaOBr at 70° to CHBr_3 and *1:4-dimethylcyclohexane-1-carboxylic acid*, b.p. 135°/14 mm. (*amide*, m.p. 127—128°).

J. W. B.

Pinacols derived from *o*-hydroxyacetophenones. W. BAKER and J. C. MCGOWAN (J.C.S., 1937, 559—562).—Reduction of *5-hydroxy-6-acetylhydriindene* [*5-O-Ac derivative* (I), m.p. 88°] with Zn dust—4% aq. NaOH gives *6-(5-hydroxyhydriindyl)methylpinacol* (II), m.p. 122°, converted by Ac_2O into (I). (II) in aq. COMe_2 —10% KOH with CH_2SO_4 affords *4:4'-bis-(4-methyl-6:7-trimethylene-1:3-benzdioxinyl)* (III), m.p. 172°. Similar reduction of *1:3:4-C₆H₃MeAc-OH* affords a mixture of stereoisomerides,

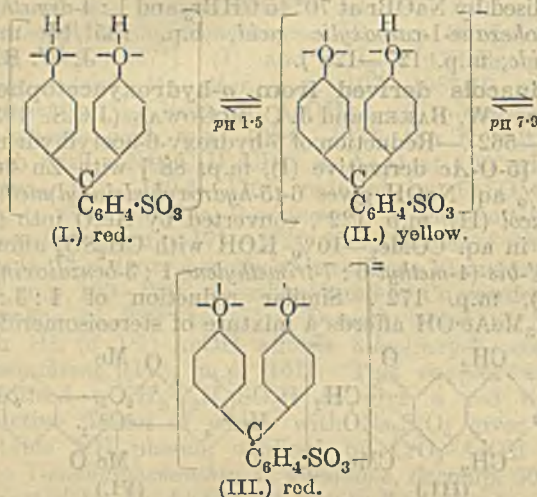


separated by boiling EtOH into the α - (? dl) (IV), m.p. 273° (decomp.) (less sol., 20% yield), and β - (? meso)-*4-hydroxy-m-tolylmethylpinacol* (V), m.p. 170° (decomp.) (from the mother-liquor; 60% yield). When heated in glacial AcOH the α -compound is converted into α -*2:3:5:5'-tetramethylcoumarano-3':2':2:3-coumaran* (VI), m.p. 151°, but the β -compound with boiling HCl-EtOH gives a mixture of (VI) and (?) a stereoisomeride of higher m.p. Methylenation of (IV) and (V) gives, respectively, α -, m.p. 243°, and β -*4:4'-bis-(4:6-dimethyl-1:3-benzdioxinyl)*, m.p. 134—135°.

J. W. B.

Molecular resonance systems. I. General. G. SCHWARZENBACH, M. BRANDENBERGER, G. H. OTT, and O. HAGGER. II. Preparation and properties of substituted anilinesulphonephthaleins. G. SCHWARZENBACH, G. H. OTT, and O. HAGGER (Helv. Chim. Acta, 1937, 20, 490—498, 498—513).—I. Resonance systems are defined as mols. in which two or more types of electron distribution are possible. The ionised carboxyl represents a symmetrical system $\text{O}=\text{CR}-\text{O}^- \rightleftharpoons ^-\text{O}-\text{CR}=\text{O}$ whereas CO_2H is an unsymmetrical system $\text{O}=\text{CR}-\text{O}-\text{H} \rightleftharpoons ^-\text{O}-\text{CR}=\text{O}-\text{H}$. Such simple resonance systems

are formed particularly by C and N. They are readily studied with dyes in which the absorption of light is intimately connected with the resonance. In them a large no. of π electrons is distributed over the whole or greater part of the mol. in such a manner that independent oscillation is excluded, thus causing absorption in the region of longer λ . Dyes are resonance systems in which two or more groups with free pairs of electrons (auxochromes) are united to an unsaturated C skeleton (chromophor) in such a manner that double linkings can be displaced without considerable modification of the stability of the mol. The acidity relationships of dyes with two-sided resonance systems are investigated with respect to phenolsulphonephthalein (I) (phenol-red). Removal of the first proton transforms the symmetrical into the unsymmetrical resonance (II), whilst departure of the second proton leads to the symmetrical form. Since resonance is causative of colour it is



immediately obvious that dissociation is accompanied by colour change. In consequence of the longer resonance chains the symmetrical forms invariably absorb in regions of longer λ than the unsymmetrical forms. With regard to acidity, the free electron pairs of the auxochromes can participate in the resonance or be impeded by a proton. The tendency of such a pair to add a proton is less on account of the resonance demand, which has a very marked influence. The dissociation consists of such indicators are therefore governed by the normal acidity of the acidic group and the difference in energy of the two resonance systems which pass into one another. The stepwise dissociation of (I) is conditioned not only by the charge remaining on the mol. after loss of the first proton but also electronically. The new $-\text{O}-$ group formed by loss of the first proton is a much better source of electrons for the central C than is the residual OH. The unsymmetrical resonance of (II) is very similar to that of a quinone. Almost the complete electron pair is provided from the one side. Discharge of the remaining OH by resonance causes diminution of its acidity. The dissociation stages of amilinesulphonephthalein are precisely similar to those of (I).

Consideration of similar dyes shows increasing stability of the resonance system in the following series of auxochromes: $\text{F}\cdot\text{NH}_2$, $\text{F}\cdot\text{OH}$, $\text{F}\cdot\text{OMe}$, $\text{F}\cdot\text{NH}_2$, $\text{F}\cdot\text{O}-$, $\text{F}\cdot\text{NH}$ ($\text{F} = \text{dye}$). Annihilation of the resonance system occurs when the central atom does not receive sufficient electrons from the auxochromes and is obliged to satisfy its demand from outside the mol. Such electrons are commonly acquired from OH' present in aq. solutions [conversion of $\text{CPh}(\text{C}_6\text{H}_4\text{X})_2$ into $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\text{X})_2$] or from CN' , $\text{SO}_3\text{H}'$, or H' .

II. (I) when heated with the substituted aniline at about 200° is transformed into substituted *anilinesulphonephthaleins*, $\text{SO}_3\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NHR})_2$, in which $\text{R} = o\text{-tolyl}$, $2:4\text{-dimethylphenyl}$, $2:4:5\text{-trimethylphenyl}$, $p\text{-anisyl}$, and $p\text{-ethoxyphenyl}$. The compounds in which $\text{R} = \text{H}$, Me , or Et are derived similarly with NH_3 and primary aliphatic amines. Very protracted heating leads to production of the corresponding leuco-compounds. Attempts to obtain chlorobenzenesulphonephthalein from PhCl and $o\text{-C}_6\text{H}_4\text{SO}_2\text{O}$ were unsuccessful, whilst the interaction of (I) and PCl_5 gives non-homogeneous phosphoric esters transformed by a small excess of the requisite amine in EtOH at 100° into *anilinesulphonephthaleins* in which $\text{R} = \text{Pr}^a$, Bu^b , $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot$, $\cdot\text{CH}_2\text{Ph}$, $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot$, $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot$, $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot$, and $o\text{-C}_6\text{H}_4\text{Br}\cdot$. The Ac_2 derivative of (I) with a large excess of the requisite amine in EtOH at 100° yields *anilinesulphonephthaleins* in which $\text{R} = 2:4\text{-C}_6\text{H}_3\text{Cl}_2\cdot$, $m\text{-C}_6\text{H}_4\text{Ac}\cdot$, $\text{C}_6\text{H}_4\text{Ph}\cdot$, $\text{NHBz}\cdot$, $\text{NMe}_2\cdot$, $\text{NEt}_2\cdot\text{C}_2\text{H}_4\cdot$, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot$, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot$. In the first two methods condensation proceeds in two distinct stages but the primary product is exceedingly reactive and could not be isolated. In all three methods N_2H_4 and $\text{NHPh}\cdot\text{NH}_2$ behave solely as reducing agents. The dyes are generally cryst., very sparingly sol. in H_2O , freely sol. in EtOH . All have indicator nature which is fully discussed from the viewpoint of Part I. They are readily brominated in AcOH (*tetrabromo-* and *tetrabromo-N-ethyl-anilinesulphonephthalein*). They give freely sol. sulphonic acids (amorphous *Ba* and *Ca* salts) which are non-homogeneous.

H. W.

Constituents of plant seedlings. I. New compounds from the unsaponifiable matter of wheat-germ oil. P. KARRER and H. SOLOMON (Helv. Chim. Acta, 1937, 20, 424—436).—Sitosterols are removed as far as possible by treatment of the unsaponifiable matter with MeOH and the residue is analysed chromatographically (Al_2O_3), thereby giving results closely similar to those of Drummond *et al.* (A., 1935, 418, 1551). The materials in layer C (probably corresponding with vitamin-E) are transformed by digitonin in 95% EtOH into apparently amorphous digitonides, which separate slowly and are considerably more sol. than those of the usual phytosterols. They are decomposed by hot abs. EtOH , thus leading to the isolation of α - (I), m.p. $114\text{--}115^\circ$, $[\alpha]_D^{20} +54.3^\circ$ in EtOH , and β - (III), m.p. 97° , $[\alpha]_D^{20} +49.2^\circ$ in EtOH , *tritisterol* and small amounts of an unnamed substance (II), m.p. 162--

163°. (I) and (II) usually separate from solvents as gels which are converted into crystals within a few hr. Their behaviour in the Liebermann and Salkowsky reactions differs completely from that of known sterols. (I) gives an *acetate*, m.p. 107—108°, $[\alpha]_D^{20} + 70.4^\circ$ in CHCl_3 , and a *dinitrobenzoate*, m.p. 182° [a second *dinitrobenzoate*, m.p. 154—155°, is formed when crude (I) is used]. (II) affords an *acetate*, $[\alpha]_D^{20} + 55.5^\circ$ in CHCl_3 , and a *dibromide*, m.p. 160—162°. (I), (II), and (III) are monohydric alcohols with at least one double linking. They are isomeric or very closely related in composition. They are regarded provisionally as $\text{C}_{30}\text{H}_{50}\text{O}$ and are thus isomeric with amyrin, to which they are very similar in many respects. H. W.

Subsidiary sterols from yeast. IV. Cryptosterol. H. WIELAND, H. PASEDACH, and A. BALLAUF (Annalen, 1937, 529, 68—83; cf. A., 1931, 1154).—From the residues of the technical prep. of ergosterol the isolation of cryptosterol (I), $\text{C}_{30}\text{H}_{50}\text{O}$, m.p. 138—140°, $[\alpha]_D^{20} + 58.7^\circ$ in CHCl_3 , is best effected by adsorption by Al_2O_3 . The composition is confirmed by analysis of the *dibromide* (II), m.p. 180—182° (decomp.), *acetate* (III), m.p. 132—134°, $[\alpha]_D^{20} + 63.7^\circ$ in CHCl_3 , and its *dibromide*, m.p. 165—167°, $[\alpha]_D^{20} + 32.8^\circ$ [re-converted into (III) by Zn dust and AcOH in boiling EtOH], *phenylurethane*, m.p. 166—168°, *benzoate*, m.p. 138—140°, $[\alpha]_D^{20} + 70.5^\circ$ in CHCl_3 , and its *dibromide*, m.p. 209—210°, and *dinitrobenzoate*, m.p. 211—212°. The presence of a double linking in (I) is established by the production of (II) and the formation (H_2 -PtO₂ in EtOH, Et₂O, or EtOAc) of *dihydrocryptosterol* (IV), $\text{C}_{30}\text{H}_{52}\text{O}$, m.p. 145—146°, $[\alpha]_D^{21} + 53.9^\circ$ in CHCl_3 {*acetate* (V), m.p. 119—120°, $[\alpha]_D^{20} + 52.9^\circ$ in CHCl_3 ; *benzoate* (VI), m.p. 190—191°, $[\alpha]_D^{20} + 72^\circ$ in CHCl_3 }. Further addition of these reactants cannot be effected, but the presence of a second double linking in (I) is established by the coloration given by (IV) and $\text{C}(\text{NO}_2)_4$ and by the conversion of (IV) by BzO_2H into its *oxide*; analogously (V) and (VI) yield *oxides*, m.p. 143°, $[\alpha]_D^{21} + 1.7^\circ$ in CHCl_3 , and m.p. 193—194°, $[\alpha]_D^{21} + 21.8^\circ$ in CHCl_3 , respectively, which do not give a colour with $\text{C}(\text{NO}_2)_4$. (I) is therefore a doubly unsaturated alcohol with four isocyclic rings. The *sec.* nature of the OH is established by the oxidation (CrO_3) of (I) to *cryptostadienone*, m.p. 65.5—67°, $[\alpha]_D^{19} + 76.3^\circ$ in CHCl_3 {*semicarbazone*, m.p. 215—225° (decomp.)}, transformed by HCl in EtOH into *chlorocryptostenone*, m.p. 134.5—136.5°, $[\alpha]_D^{20} + 69.1^\circ$. (The nomenclature is based on the term "cryptostane" for the parent hydrocarbon.) Further, (IV) [cryptostenol] is oxidised to *cryptostenone*, $\text{C}_{30}\text{H}_{50}\text{O}$, m.p. 117—118°, $[\alpha]_D^{19} + 61.3^\circ$ in CHCl_3 , the *semicarbazone*, m.p. 220—224°, of which is transformed by NaOEt and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in EtOH at 200° into *cryptostene*, $\text{C}_{30}\text{H}_{52}$, m.p. 74.5—76°, $[\alpha]_D^{19} + 60.1^\circ$ in CHCl_3 . (I) differs from other sterols in composition and colour reaction with H_2SO_4 - Ac_2O but resembles them in yielding a *digitonide*. It very closely resembles but is not identical with lanosterol (VII). In constitution it appears to belong to the unexplored group of triterpene alcohols. Epimerisation of (I) or (VII) could not be achieved but epimerism is not the sole

cause of the difference between them since the corresponding ketones also differ from one another.

H. W.

Sterols, $\text{C}_{25}\text{H}_{42}\text{O}$, m.p. 142—143°, $[\alpha]_D^{32} + 16.24^\circ$ in CHCl_3 , and (?) $\text{C}_{24}\text{H}_{40}\text{O}$, m.p. 122°, $[\alpha]_D^{32}$ (?) —83.45° in CHCl_3 .—See A., III, 190.

Sexual hormones. XXII. Preparation of Δ^5 -3-epihydroxy-17-transhydroxyandrostene and 3-epihydroxy-17-transhydroxyætiocolane. L. RUZICKA, M. W. GOLDBERG, and W. BOSSHARD (Helv. Chim. Acta, 1937, 20, 541—547).— Δ^5 -Androstene-3:17-diol 17-monopropionate in AcOH is treated successively with Br and CrO_3 and the product is debrominated by Zn dust in boiling MeOH to (impure) Δ^5 -testosterone propionate (I), m.p. (indef.) 135°, $[\alpha]_D - 17^\circ$ in EtOH. (I) is hydrogenated (Raney Ni in 95% EtOH) and the product after treatment with digitonin, is hydrolysed to Δ^5 -3-epihydroxy-17-transhydroxyandrostene (II), m.p. 208—209°, $[\alpha]_D - 54^\circ \pm 2^\circ$ in EtOH (*diacetate*, m.p. 155—155.5°). Alternatively (II) is obtained by reduction (Raney Ni in 95% EtOH) of Δ^5 -3-epihydroxyandrostene-17-one. Δ^6 -Androstene-3:17-diol 17-monobenzoate is brominated, oxidised, and then debrominated to Δ^5 -testosterone benzoate, m.p. (indef.) 170—180°, $[\alpha]_D + 23^\circ$ in C_6H_6 (Δ^4 -testosterone benzoate has $[\alpha]_D + 143^\circ$ in C_6H_6), which is reduced (Raney Ni in dioxan) to 3-epihydroxy-17-transhydroxyætiocolane, m.p. 236—236.5°, $[\alpha]_D + 25^\circ \pm 1.5^\circ$ in EtOH (*diacetate*, m.p. 124.5—125.5°), the constitution of which is established by its identity with the product obtained by hydrogenation (Ni or Pt) of 3-epihydroxyætiocolan-17-one. It is identical with the product isolated by Butenandt from male urine. H. W.

Separation of the C_{17} -epimers of œstradiol by digitonin. O. WINTERSTEINER (J. Amer. Chem. Soc., 1937, 59, 765).— α -œstradiol (I), m.p. 178°, $[\alpha]_D + 81^\circ$ in 80% EtOH, rapidly forms a *digitonide*, m.p. about 265° (decomp. from 195°) (readily regenerates the diol); β -œstradiol, m.p. 228°, $[\alpha]_D + 54^\circ$, is readily obtained from the mother-liquors. The 3-benzoate of (I) gives a *digitonide* more slowly. Digitonide formation is not an infallible guide to structure. R. S. C.

Iodinating properties of the complex of iodine and silver benzoate. C. PRÉVOST and J. WIEMANN (Compt. rend., 1937, 204, 700—701).—This complex (A., 1935, 738) with $\text{CR}:\text{Cag}$ gives $\text{CR}:\text{CI}$ and AgOBz , and with MgRBr gives AgBr and $\text{Mg}(\text{OBz})_2$. From PhOH , some $\text{C}_6\text{H}_5\text{I}_3 \cdot \text{OH}$ is formed; H_2O gives AgOI (or $2\text{AgI} + \text{AgIO}_3$), and AcOH yields a complex mixture of products. E. W. W.

Synthesis of new local anaesthetics. I. K. N. GAIND (J. Indian Chem. Soc., 1937, 14, 13—16).—Compounds of type $\text{NET}_2 \cdot \text{CHR}'\text{CMe}(\text{OBz})\text{CO}_2\text{R}$ are prepared, and found to have local anaesthetic action. The cyanohydrin (I) of chloroacetone (II) [improved prep. of (I) from the NaHSO_3 derivative of (II)] is hydrolysed to β -chloro- α -hydroxyisobutyric acid (III), of which the CH_2Ph ester, b.p. 185°/45 mm., is condensed with NH_4Et (in C_6H_6 at 150°), followed by benzoylation of the resulting *base*, to give *benzyl*

β -diethylamino- α -benzoyloxyisobutyrate, m.p. 63° (hydrochloride, m.p. 198°). The hydrochloride, m.p. 195°, of the α -p-nitrobenzoyloxy-compound is similarly prepared, and is reduced ($\text{PtO}_2\text{-H}_2$) to the hydrochloride, m.p. 175°, of the α -p-aminobenzoyloxy-compound. The Pr^a , b.p. 100°/13 mm., and Pr^b , b.p. 110°/12 mm., esters of (III) give respectively Pr^a , m.p. 56° (hydrochloride, m.p. 217°), and Pr^b β -diethylamino- α -benzoyloxyisobutyrate, m.p. 44° (hydrochloride, m.p. 207°). From Me α -chloroethyl ketone (IV), β -chloro- α -hydroxy- α -methylbutyric acid is prepared (through the nitrile), and thence the CH_2Ph ester (V), b.p. 180°/20 mm., from which benzyl β -dimethylamino- α -benzoyloxy- α -methylbutyrate (VI), m.p. 61° (hydrochloride, m.p. 207°), is obtained. If (IV) is not pure, (V) is accompanied by an isomeride, b.p. 210°/20 mm., giving an isomeride, m.p. 47° (hydrochloride, m.p. 235°), of (VI). E. W. W.

Electrochemical oxidation of 2:4-dimethylbenzonitrile. F. FIGHTER and G. SCHETTY (Helv. Chim. Acta, 1937, 20, 563—567).—Electrolysis of 2:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CN}$ in 0.5N- H_2SO_4 with a Pb anode and Sn cathode but without diaphragm gives 2:4-dimethylbenzylamine (Bz derivative, m.p. 97.5—98°). When a diaphragm is used, the sole product of the oxidation is 6-cyano-*m*-toluic acid (I), m.p. 220° (corr.). The yield is >12% with anode c.d. 0.03 amp. per sq. cm.; increase of c.d. causes resinification whereas a purer product is obtained in poorer yield if c.d. is decreased. (I) [Cd (+6 H_2O) salt; Me ester, m.p. 81°] is obtained from 6-amino-*m*-toluic acid and is hydrolysed to 2-methylterephthalic acid. H. W.

Manufacture of (A) N-aminoalkylanthranilic acid alkyl esters; (B) N-aminoalkylamides of alkylaminobenzoic acids. [Local anæsthetics.]—See B., 1937, 327.

Syntheses with magnesium [derivative of] sodium phenylacetate. V. ALIPHATIC ORGANO-MAGNESIUM DERIVATIVES. D. IVANOV (Bull. Soc. chim., 1937, [v], 4, 682—686).— $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$ reacts with Mg alkyl halides by the same mechanism as $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{MgCl}$ reacts with Mg aryl bromides (A., 1931, 726) to give $\text{CH}_2\text{Ph}\cdot\text{CR}(\text{OH})\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ in 20—55% yields, and thus from the appropriate MgRX are obtained β -hydroxy- α -diphenyl- β -ethyl-, m.p. 135—145° (Me ester, m.p. 81—83°) (also synthesised from $\text{MgCl}\cdot\text{CHPh}\cdot\text{CO}_2\text{Na}$ and $\text{CH}_2\text{Ph}\cdot\text{COMe}$), β -*n*-propyl-, m.p. 152—160°, β -*n*-butyl-, m.p. 115—120°, and β -isoamyl-, m.p. 166—168°, -butyric acid. Hydrolysis of these acids gives good yields of the ketones $\text{R}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$. Na *p*-chlorophenylacetate behaves similarly, but only very small yields are obtained with the *o*-Cl-compound. $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{MgCl}$ and MgEtBr or MgPr^aBr similarly afford a mixture of acids in yields >11%, from which $\text{CH}_2\text{Ph}\cdot\text{COEt}$ (semicarbazone, m.p. 153°; lit. m.p. 133.5°) and $\text{CH}_2\text{Ph}\cdot\text{COPr}^a$ are obtained on hydrolysis.

J. W. B.

Derivatives of benzoylbenzoic acids. I. 2-(2'- and 2-(4'-hydroxybenzoyl)-3-methylbenzoic acid and 2-(4'-chlorobenzoyl)-3-methylbenzoic acid. II. 2-Benzoyl-3-methylbenzoic acid and 2-benzoyl-6-methylbenzoic acid. M. HAYASHI and S. TSURUOKA. III. 3(6?)-Nitro-2-benzoyl-

benzoic acid, 3(6?)-nitro-2-[2'(4?)-hydroxybenzoyl]benzoic acid, 3(6?)-nitro-2-(2':5'-dimethylbenzoyl)benzoic acid and 5(4?)-nitro-2-(2':5'-dimethylbenzoyl)benzoic acid. M. HAYASHI, S. TSURUOKA, and A. NAKAYAMA (J. Chem. Soc. Japan, 1935, 56, 1031—1034, 1084—1092, 1093—1101).—I. 3-Methylphthalic anhydride (I) and PhOH afford 2-(2'-, m.p. 220—221°, and 2-(4'-hydroxybenzoyl)-, m.p. 197—198°, -3-methylbenzoic acid, converted into the isomeric 6-Me derivatives, m.p. 141—142° and m.p. 183—184°, by conc. H_2SO_4 . (I) and PhCl afford 2-(4'-chlorobenzoyl)-3-methylbenzoic acid, m.p. 175.5—176°.

II. (I) and C_6H_6 afford 2:3-dibenzoyltoluene, m.p. 116—117°, and 2-benzoyl-6-, m.p. 126—127.5°, and 3-, m.p. 171—172°, -methylbenzoic acid, oxidised (KMnO_4) to benzophenone-2:6-, m.p. 225—226°, and 2:3-, m.p. 121—125°, -dicarboxylic acid, respectively; the 3-derivative is converted into the 6-Me isomeride with hot conc. H_2SO_4 .

III. The following are prepared by the Friedel-Crafts reaction: 3(6?)-nitro-, m.p. 236—237°, and 6(3?)-nitro-, m.p. 160—161°, -2-benzoylbenzoic acids; 4(5?)-nitro-2-(2':5'-dimethylbenzoyl)benzoic acid, m.p. 191.5—192.5°. CH. ABS. (r)

1:2- and 1:4-Addition. I. 1:4-Addition of potassium isocyanide. A. MICHAEL and N. WEINER (J. Amer. Chem. Soc., 1937, 59, 744—753).—The following reactions are interpreted in accordance with Michael's general views as proving 1:4-addition of KNC (KCN) to $\alpha\beta$ -unsaturated ketones, esters, and nitriles, the primary products being K enolates or iminolates, which, if "poorly neutralised," react further with unchanged esters etc. Other views are held to be disproved. Allyl cyanide and KNC in dry MeOH do not react. $\text{CHPh}\cdot\text{C}(\text{CO}_2\text{Me})_2$ and KNC in dry MeOH give a K enolate, which with acid gives quantitatively Me_2 β -cyanobenzylmalonate (I), m.p. 47.5—48.5°, obtained also in poor yield in aq. MeOH. The K enolate with CH_2PhBr in PhMe gives Me_2 β -cyano- α -benzylbenzylmalonate, m.p. 117.5—118°, converted into $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ by HCl at 200°, and with I gives equal amounts of (I) and Me_2 β -cyanobenzylidenemalonate, m.p. 74°, hydrogenated to (I) and converted by KNC in dry MeOH into a K derivative, which with acid gives Me $\alpha\beta$ -dicyano- β -phenylpropionate, m.p. 107—108°, also obtained by I with Me $\alpha\beta$ -dicyano- β -phenylacrylate, m.p. 87—88°. Me_2 fumarate and KNC in aq. MeOH give $\text{CO}_2\text{Me}\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ (II), $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$, and Me_2 δ -cyano-*n*-butane- $\alpha\beta\gamma$ -tricarboxylate (III), b.p. 178—180°/3 mm. (converted by hydrolysis and dehydration into butane- $\alpha\beta\gamma\delta$ -tetracarboxylic acid and its dianhydride); in cold abs. MeOH (II) and Me_2 2-cyanocyclopentanone-3:4:5-tricarboxylate (IV), b.p. 196°/4 mm., are formed; in hot abs. MeOH only (IV) is obtained. The reaction is interpreted as formation by NaOMe of (II) and by KNC of $\text{CO}_2\text{Me}\cdot\text{CH}(\text{CN})\cdot\text{CH}\cdot\text{C}(\text{OMe})\cdot\text{OK}$ and thence of $\text{KNC}\cdot\text{C}(\text{CO}_2\text{Me})\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, which with unchanged Me_2 fumarate gives $\text{KNC}\cdot\text{C}(\text{CO}_2\text{Me})\cdot[\text{CH}(\text{CO}_2\text{Me})]_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, which yields (III) by saponification and loss of CO_2 and (IV) by a Dieckmann reaction. Hot HCl converts (IV)

into a substance, m.p. $>300^\circ$, which with amyl nitrite gives cyclopentanone-3:4-dicarboxylic acid. Me_2 citraconate reacts with KNC after isomerisation to the itaconate; in cold, dry MeOH Me_2 γ -methoxy-methylsuccinate, b.p. $80.5^\circ/1$ mm. (also obtained by NaOMe; corresponding acid, new m.p. $102-103^\circ$), and carbomethoxymethyl-succinimide or -imidolactone, m.p. $80-81^\circ$, b.p. $167-175^\circ/1$ mm. (gives tricarballylic acid when hydrolysed), are formed; when heated, only the lactone is obtained.

$\text{CHPh}:\text{CH}:\text{COPh}$ and KNC in dry MeOH give $\text{Ph}_2\beta$ -cyano- $\beta\beta'$ -tetramethylene diketone (V), m.p. 237° , converted by CrO_3 -AcOH or NaOH-50% EtOH into the substance, $\text{C}_{31}\text{H}_{23}\text{ON}$ (Hann *et al.*, J.C.S., 1904, 85, 1358); with Br (V) gives HBr and a substance, $\text{C}_{31}\text{H}_{22}\text{ONBr}$, m.p. $188-189^\circ$, converted by NaOMe into a substance, $\text{C}_{31}\text{H}_{21}\text{ON}$, m.p. 188° , which with CrO_3 gives a substance, $\text{C}_{22}\text{H}_{17}\text{ON}$, m.p. $235-237^\circ$ (decomp.). $\text{CHPh}:\text{CH}:\text{C}(\text{CO}_2\text{Me})_2$ and KNC in dry MeOH give a substance, $\text{C}_{22}\text{H}_{20}\text{O}_8\text{N}$, m.p. $143-144^\circ$; new interpretations are given of the reactions observed by other workers. Me crotonate gives a complex mixture by secondary reactions.

$\text{CPh}:\text{C}:\text{CO}_2\text{Me}$ and KNC in dry MeOH give $\text{CH}_2\text{Br}:\text{C}:\text{CO}_2\text{Me}$ and $\text{CN}:\text{CHPh}:\text{CH}(\text{CN})\cdot\text{CO}_2\text{Me}$ (obtained as main product in aq. MeOH); the intermediates are successively $\text{CN}:\text{CPh}:\text{C}(\text{OMe})\cdot\text{OK}$ and $\text{NK}:\text{C}:\text{CPh}:\text{C}(\text{CO}_2\text{Me})\cdot\text{C}:\text{NK}$. R. S. C.

Preparation of β -4-methoxy-1-naphthoylepropionic acid. K. P. DAVE and K. S. NARGUND (J. Indian Chem. Soc., 1937, 14, 58).—This acid (A., 1932, 948) (*Me*, m.p. 56° , and *Et*, b.p. $230^\circ/15$ mm., esters) is obtained in much increased yield by using PhNO_2 or $(\text{CHCl}_2)_2$ as solvent. Its constitution is established by prep. from the 4-bromo- α -naphthyl Me ether Grignard reagent and succinic anhydride.

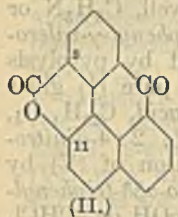
E. W. W.

Substituted succinic acids. II. Conversion of α' -diarylsuccinamides into diarylacetic acids. J. A. McRAE, W. C. CONN, and K. J. PLATT (Canad. J. Res., 1937, 15, B, 46-51).— p - $\text{C}_6\text{H}_4\text{Me}:\text{CH}:\text{CPh}:\text{CN}$ with EtOH-KCN- NH_4Cl gives α -phenyl- α' - p -tolylsuccinidinitrile, m.p. 195° , hydrolysed by 85% H_2SO_4 at 100° to the diamide (I), m.p. 294° (corr.) (decomp.), and α -phenyl- α' - p -tolylsuccinic acid, m.p. 224° (*Et*, ester, m.p. 97°). By similar methods are obtained α -phenyl- α' - p -chlorophenylsuccinidinitrile, m.p. 225° , and -diamide (II), m.p. 296° (corr.), and -succinic acid, m.p. $240-241^\circ$; also α -phenyl- α' - p -bromophenylsuccinidinitrile, m.p. $213-214^\circ$ (corr.), and -diamide (III), m.p. $300-301^\circ$ (corr.) (decomp.). Like the unsubstituted derivative (A., 1935, 212) (I), (II), and (III) are converted by NaOBr into $\text{CHAr}_2\cdot\text{CO}_2\text{H}$ which are difficult to purify and were isolated and identified as anilides; thus are obtained phenyl- p -tolyl-, m.p. $154-155^\circ$, phenyl- p -chlorophenyl-, m.p. 179° [acid synthesised from p - $\text{C}_6\text{H}_4\text{Cl}:\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ and C_6H_6 with SnCl_4], and phenyl- p -bromophenyl-, m.p. $177-178^\circ$, -acetanilide. J. W. B.

Action of alkaline reagents on diphenylbenzoylbutyrolactone [δ -keto- $\alpha\beta\delta$ -triphenyl- γ -valerolactone]. C. F. H. ALLEN, E. E. MASSEY, and R. V. V. NICHOLLS (J. Amer. Chem. Soc., 1937, 59, 679-686).—The mixture of Me δ -keto- $\alpha\beta\delta$ -triphenyl-

valerates, obtained from $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Me}$, $\text{COPh}:\text{CH}:\text{CHPh}$, and NaOMe, with Br-AcOH or $-\text{CCl}_4$ gives isomeric forms, (I) m.p. 176° , (II) m.p. 158° , (III) m.p. 147° , and (IV) m.p. 120° [constant-melting mixture of (II) and (III) has m.p. 125°], of Me γ -bromo- δ -keto- $\alpha\beta\delta$ -triphenylvalerate. (I) and (II) are unchanged by cold HBr-AcOH, but (III) gives (II), and (IV) gives (I). The naturally obtained mixture with KOAc-AcOH or, less well, $\text{C}_5\text{H}_5\text{N}$ or NPhMe_2 gives 65% of δ -keto- $\alpha\beta\delta$ -triphenyl- γ -valerolactone (V), m.p. 157° , also obtained by pyrolysis with other substances; pyrolysis of pure (I) gives 80% of MeBr, (V), and a (?) diketone-acid, $\text{C}_{23}\text{H}_{18}\text{O}_4$, m.p. 160° (phenylhydrazone, m.p. 180° ; 2:4-dinitrophenylhydrazone, m.p. 210°). Reduction of (V) by Zn dust-AcOH or -MeOH gives δ -keto- $\alpha\beta\delta$ -triphenylvaleric acid, m.p. 187° , but by HBr-AcOH or $-\text{CHCl}_3$ a form (VIII) thereof, m.p. 261° . NH_3 -EtOH and (V) give slowly γ -hydroxy- δ -keto- $\alpha\beta\delta$ -triphenylvaleramide, decomp. 202° , converted by HCl-MeOH into 2-benzoyl-1:3-diphenylcyclopropane-1-carboxylamide and regenerated therefrom by H_2SO_4 - Ac_2O . $\text{Mg}(\text{OMe})_2$ -MeOH hydrolyses (V) to Me γ -hydroxy- δ -keto- $\alpha\beta\delta$ -triphenylvalerate, forms, (VIII) m.p. 180° (acetate, m.p. 145°) and (IX) m.p. 145° [converted into (VIII) by cold $\text{Mg}(\text{OMe})_2$; acetate, m.p. 132°], but simultaneous reduction also occurs. (VIII) and (IX) regenerate (V) at 190° . With $\text{NPh}:\text{NH}_2$ (VII) gives its phenylhydrazone, m.p. 224° , but (IX) gives that of (V); the two hydrazones are interconvertible by a little HCl, the former being obtained in hot MeOH, the latter in hot CHCl_3 . NaOMe converts (V) into 1:2:4-triphenyl- Δ^1 -cyclopentene-3:5-dione (X), m.p. 166° (2:4-dinitrophenylhydrazone, m.p. 235°), (VII), $(\text{CPh}:\text{CO})_2\text{O}$, $(-\text{CHPh}:\text{CO}_2\text{H})_2$, m.p. 229° , γ -benzylidene- $\alpha\beta$ -diphenyl- γ -crotonolactone (XI), PhCHO, and other products [decomposing when distilled/vac. into BzOH, $(\text{CHPh})_2$, and COPhMe]. The conversion of (XI) into γ -hydroxy- $\alpha\beta\delta$ -triphenylvalero- γ -lactone (XII) and dehydration thereof are modified. KOH-EtOH converts (X) or (XI) into PhCHO and $(\text{CPh}:\text{CO})_2\text{O}$; with NaOEt (XI) gives (X) slowly. NH_3 -EtOH and (X) at 100° give the lactam of γ -amino- $\alpha\beta\delta$ -triphenyl- $\Delta^{\alpha\gamma}$ -butadiene- α -carboxylic acid and γ -keto- $\alpha\beta\delta$ -triphenyl- Δ^{α} -pentene- α -carboxylamide, also obtained similarly from (XI). (X) is stable to KOB or Br, with dil. HNO_3 gives oils and p - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, with KMnO_4 gives PhCHO, BzOH, and CO_2 , and with SeO_2 in hot dioxan gives a bimol. product, $\text{C}_{48}\text{H}_{30}\text{O}_4$, m.p. 247° , also obtained with PhCHO and BzOH by CrO_3 or O_3 in EtBr; alkaline H_2O_2 gives a substance, (?) $\text{C}_{23}\text{H}_{18}\text{O}_3$, m.p. 185° , which yields a (?) dehydrated diacetate, $\text{C}_{50}\text{H}_{24}\text{O}_7$, m.p. 155° . $\text{CO}(\text{CH}_2\text{Ph})_2$, BzCO₂Et, and NaOEt (1 mol.) give 27% of (XI) and some (XII); NaOMe as catalyst gives 40% of (II), whereas piperidine or a trace of NaOEt yields Et α -hydroxy- γ -keto- $\alpha\beta\delta$ -triphenylvalerate, m.p. 128° (acetate, m.p. 101°). The mechanism of the complex changes is discussed. Formation of (X) probably occurs by hydrolysis of (V) to $\text{CO}_2\text{H}:\text{CHPh}:\text{CHPh}:\text{CH}(\text{OH})\cdot\text{COPh}$, isomerisation thereof to $\text{CO}_2\text{H}:\text{CHPh}:\text{CHPh}:\text{CO}:\text{CHPh}:\text{OH}$, and conversion successively into $\text{CO}_2\text{H}:\text{CHPh}:\text{CHPh}:\text{CO}:\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{H}:\text{CPh}:\text{CPh}:\text{CO}:\text{CH}_2\text{Ph}$. R. S. C.

Oxidation products of benzanthrone-8-carboxylic acid. J. L. GRIEVE and H. G. RULE (J.C.S., 1937, 535—537).—*Me* 8-bromo-7-methoxy-1-naphthoate, m.p. 79° (from the acid through the acid chloride), with $o\text{-C}_6\text{H}_4\text{I}\cdot\text{CO}_2\text{Me}$ and Cu-bronze at 175° gives *Me* 7-methoxy-8-(*o*-carbomethoxyphenyl)-1-naphthoate (I), m.p. 137°, hydrolysed by KOH-EtOH to the corresponding acid, m.p. 239°. (I) with conc. H_2SO_4



at room temp. gives a theoretical yield of the lactone (II) of 11-hydroxybenzanthrone-8-carboxylic acid, identical with the specimen obtained (A., 1935, 859) by oxidation of benzanthrone-8-carboxylic acid (III) with hot conc. H_2SO_4 . The close proximity of the 8:11 positions greatly favours the formation of (II) since only with $\text{H}_2\text{SO}_4\text{-AcOH}$ at 80° can a small yield [with much (II)] of the intermediate *Me* 11-methoxybenzanthrone-8-carboxylate, m.p. 194°, be obtained. This is converted into (II) even by alkaline hydrolysis. Oxidation of (III) with boiling $\text{KMnO}_4\text{-NaOH}$ gives a small yield of anthraquinone-1:8-dicarboxylic acid, m.p. 316—317° (decomp.), decarboxylated (Cu-bronze) to anthraquinone. J. W. B.

Bile acids. LI. M. SCHENCK (Z. physiol. Chem., 1937, 246, 258—266; cf. this vol., 20).—The acid $\text{C}_{24}\text{H}_{34}\text{O}_{10}\text{N}_2$ (Schenck and Kirchhof, A., 1929, 558) with NaOH-KMnO_4 at room temp. yields a tetrabasic acid, $\text{C}_{24}\text{H}_{35}\text{O}_{10}\text{N}_2$, decomp. 195°, similarly afforded by the ketolactamtricarboxylic acid (I) (A., 1936, 74). Both bilianic acid (II) and the acid $\text{C}_{24}\text{H}_{33}\text{O}_{10}\text{N}_2$, similarly treated, yield cilianic acid. For controlling the oxidation of (I) or (II) by HNO_3 , $\text{NH}_2\cdot\text{SO}_3\text{H}$ is substituted for $\text{CO}(\text{NH}_2)_2$ (A., 1936, 1109). The constitution of (I) derivatives is further discussed. F. O. H.

Carbocyclic compounds. XXX. Internal condensation of hexadecane- $\alpha\omega$ - and octadecane- $\alpha\omega$ -dialdehyde. M. STOLL and A. ROUVÉ (Helv. Chim. Acta, 1937, 20, 525—541).—Cyclisation of $\alpha\omega$ -dialdehydes is shown to occur when the length of chain is such that steric hindrance is not experienced and when the solution is so dil. that the mol. has opportunity to become joined at its extremities before encountering a second mol. The NaHSO_3 compound of *Me* θ -aldehydononanecarboxylate in Et_2O is decomposed by Na_2CO_3 and the product is treated with HCl-MeOH and then hydrolysed to the *Me*₂ acetal of sebacaldehydic acid. Electrolysis of the latter in MeOH affords octadecane- $\alpha\omega$ -dialdehyde *Me*₄ acetal (I), b.p. 178—185°/0.02—0.03 mm., m.p. 34—35°, from which octadecane- $\alpha\omega$ -dialdehyde (II), m.p. 50—52°, is obtained by means of boiling 10% HCl . (II) cannot be purified from an apparent trace of acid through the semicarbazone or by distillation, which is accompanied by spontaneous polymerisation. Hexadecane- $\alpha\omega$ -dialdehyde *Me*₄ acetal (III) has b.p. 164—165°/0.2 mm., m.p. 21—22°. Condensation of hexadecane- $\alpha\omega$ -dialdehyde (IV) by NaNH_2 in Et_2O containing a little EtOH gives mainly a caoutchouc-like polymeride and non-cryst. products which could not be distilled. Oxidation of the latter with Ag_2O gives a little thapsic acid. Apart from the odour of

musk there is no distinct evidence of cyclisation. Under the influence of piperidine acetate (IV) is transformed mainly into resins sol. with difficulty in Et_2O or EtOH ; the volatile portions have an odour of musk but appear to give a mixture of semicarbazones. (III) is cyclised by PhSO_3H in boiling C_6H_6 to Δ^1 -cyclopentadecene-1-aldehyde, $\text{CH}_2\text{<}\frac{\text{CH}}{[\text{CH}_2]_{13}}\text{>C}\cdot\text{CHO}$,

[semicarbazone, m.p. 147—149° (152°)], hydrogenated (Ni in EtOH) to cyclopentadecylcarbinol (V), b.p. 133—136°/0.08 mm. [3:5-dinitrobenzoate (VI), m.p. 100—101°]. Exaltone, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, and NaNH_2 in Et_2O slowly yield *Et* cyclopentadecylglycidate, hydrolysed to cyclopentadecylglycidic acid [(?) corresponding amide, m.p. 173—175°], which passes when distilled into cyclopentadecaldehyde, b.p. 108—112°/0.05 mm.; the latter substance is reduced to (V) which is identified as (VI). Attempts to cyclise (II) in alkaline media were unsuccessful but (I) is converted by PhSO_3H in boiling C_6H_6 into Δ^1 -cycloheptadecene-1-aldehyde, b.p. 130—133°/0.05 mm. [semicarbazone, m.p. 143—143.5° (corr.)], which is hydrogenated to cycloheptadecylcarbinol (VII), b.p. 160—163°/0.12 mm. [*H* phthalate; 3:5-dinitrobenzoate (VIII), m.p. 90.5—91°]. (VII) is readily transformed into the corresponding stearate, b.p. 260—270°/0.2 mm., m.p. about 25°, which could not be dehydrated. Esterification of (VII) with HBr and passage of the bromide over BaCl_2 yields an unsaturated hydrocarbon, ozonisation of which in EtOAc at -50° followed by catalytic decomp. of the ozonide appears to give a CO-aldehyde (disemicarbazone, $\text{C}_{20}\text{H}_{40}\text{O}_2\text{N}_6$, m.p. 163—165° to a cloudy liquid which becomes transparent at 167°). Direct dehydrogenation of (VII) by AlCl_3 at 310—320°/0.1 mm. affords methylenecycloheptadecane, b.p. 112—115°/0.05 mm., ozonised to a substance with a very feeble odour of musk (semicarbazone, m.p. 136—140°). Dihydrocivetone, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, and NaNH_2 in Et_2O afford *Et* cycloheptadecylglycidate, b.p. 143—150°/0.05 mm., hydrolysed to cycloheptadecylglycidic acid, which decomposes when distilled in a vac. to cycloheptadecaldehyde, b.p. 123—125°/0.05 mm. (semicarbazone, m.p. 132—135°), which is reduced to (VII), identified as (VIII). H. W.

Ethylenic aldehydes. M. MEYER (Compt. rend., 1937, 204, 508—509).— α -Ethoxy- β -styrylpropionic acid and α -ethoxy- η -vinylundecic acid (cf. this vol., 47) at 280—300° afford (cf. A., 1933, 491) cinnamyl-formaldehyde (8-phenyl- Δ^2 -butenaldehyde), b.p. 130—132°/14 mm. [semicarbazone, m.p. 212—214° (block)], and Δ^1 -dodecenaldehyde, b.p. 100—102°/3.5 mm. (semicarbazone, m.p. 91°), respectively. J. L. D.

$\alpha\beta$ -Diphenylpropaldehyde. H. BURTON and C. W. SHOFFEE (J.C.S., 1937, 546—549).— $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{COCl}$ and NH_2Ph afford $\alpha\beta$ -diphenylpropanilide, m.p. 166°, converted by PCl_5 in $\text{C}_2\text{H}_2\text{Cl}_4$ at 140° into the iminochloride, reduced (SnCl_2 , $\text{Et}_2\text{O-HCl-C}_2\text{H}_2\text{Cl}_4$) to $\alpha\beta$ -diphenylpropaldehyde (I), b.p. 170°/11 mm., m.p. 54° (semicarbazone, m.p. 124—125°; 2:4-dinitrophenylhydrazones, two forms, m.p. 148—152°, and m.p. 199°). The compound, m.p. 116°, described as the hydrate of (I) by Stoermer *et al.* (A., 1926, 160) is actually $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{OH}$ (Kohler *et al.*, A., 1934, 523; Jarrousse, A., 1936,

1252) [semicarbazone, m.p. 191—192° (decomp.); 2:4-dinitrophenylhydrazone, m.p. 164—164.5°], oxidised by Nessler's reagent in dioxan at 15° to $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{COPh}$, but with Nessler's reagent in COMe_2 it affords $\delta\epsilon$ -diketo- $\gamma\epsilon$ -diphenyl- β -methyl- Δ^2 -pentene, m.p. 123°, which with O_3 gives COMe_2 , BzOH , and BzCO_2H [characterised as 3-keto-2-phenyl-3:4-dihydroquinoxaline, m.p. 247°, which is formed with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$]. (I) could not be obtained by catalytic reduction (Adams) of $\text{CHPh}\cdot\text{CPh}\cdot\text{CHO}$, but is oxidised by Ag_2O to $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$. (I) with $\text{CH}_3(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ -piperidine affords $\gamma\delta$ -diphenyl- Δ^2 -pentenoic acid, m.p. 89°. J. W. B.

Coordinate valency rings. III. Inner complex salts of iron and manganese. T. TSUMAKI (J. Chem. Soc. Japan, 1935, 56, 1329—1331; cf. A., 1935, 750).—The Fe derivative of trisalicylaldehyde-imine (I), $\text{C}_{21}\text{H}_{15}\text{O}_3\text{N}_2\text{Fe}$, was prepared by the interaction of hot solutions of (a) 4 g. of salicylaldehyde, 10 g. of 25% aq. NH_3 , and 150 c.c. of EtOH and (b) 80 c.c. of 5.0% Fe NH_4 alum. Mn derivatives of (I) and of salicylaldehydebenzylimine (II) and the hydroxy-Mn derivative of (II) were prepared similarly. CH. ABS. (c)

Hydroxymethylene compounds. R. KELLER (Helv. Chim. Acta, 1937, 20, 436—450).—Hydroxymethylenephénylacetaldehyde (I) (20% excess) and NH_2Ph afford anilinomethylenephénylacetaldehyde (II), m.p. 137°. With 2 mols. of NH_2Ph (I) yields the anil, $\text{NHPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{NPh}$, m.p. 130°, hydrolysed by 10% HCl to (II). (I) and anthranilic acid yield o' -carboxyanilinomethylenephénylethylideneanthranilic acid, m.p. 251°, hydrolysed to o' -carboxyanilinomethylenephénylacetaldehyde, m.p. 220°, obtainable with difficulty by condensation of the components. According to conditions $p\text{-NH}_2\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ yields p' -carbethoxyanilinomethylenephénylacetaldehyde, m.p. 131°, or the Schiff's base,

$\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, m.p. 145°. (I) and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ (1:1) give 1-naphthylaminomethylenephénylacetaldehyde (III), m.p. 82°, or (1:2) β -phenyl- β -naphthylaminomethylene-ethylidene- α -naphthylamine (IV), m.p. 233°. The conversion of (III) into a semicarbazone or of (III) into (IV) could not be effected. Benzoyloxymethylenephénylacetaldehyde and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ (1:2) afford (IV) and BzOH . β -Naphthylaminomethylenephénylacetaldehyde, m.p. 282° (from the reactants in any ratio), does not react with $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$,

$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, HCl, or NH_2Ph and is stable towards boiling HCl. p -Toluidinomethylenephénylacetaldehyde has m.p. 152°. $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ and (I) yield β -phenyl- β - o' -toluidinomethylene-ethylidene- o -toluidine, m.p. 129°. α -Aminocamphor and (I) give the Schiff's base,

$\text{CO}\cdot\text{C}_9\text{H}_{14}\cdot\text{CH}\cdot\text{NH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_9\text{H}_{14}\cdot\text{CO}$, m.p. 156° (perchlorate; hydrochloride; sulphate), which exhibits complete abnormal rotation dispersion. Phenylcarbazidomethylenephénylacetaldehydephenylsemicarbazone, m.p. 216°, is obtained from (I) and $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ in all proportions. (I) and $\text{NHPh}\cdot\text{OH}$ in HCO_2H or AcOH afford diphenyliso-

oxazolone, $\text{CPh}\cdot\text{CO}\cdot\text{CH}\cdot\text{NPh}\cdot\text{O}$, m.p. 167°, hydrolysed by $\text{KOH}\cdot\text{H}_2\text{O}\cdot\text{EtOH}$ to *trans*-phenylhydroxylaminomethylenephénylacetic acid, m.p. 132°. Under somewhat different conditions the product obtained is *acetoxymethylenephénylacetanilide*, m.p. 141—142° hydrolysed to $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NHPh}$, m.p. 118°, or *N*-phenylisophénylacetaldoxime, m.p. 146°. Hydroxymethylenephénylacetonitrile in EtOH is hydrogenated (Ni on clay) under pressure to β -phenylpropylamine, b.p. 90°/13 mm. (hydrochloride; *H* oxalate, m.p. 137°; *Bz* derivative, m.p. 94°), and (?) *di*- β -phenylpropylamine, b.p. 180°/13 mm. (*H* oxalate, m.p. 216°). Condensation of (I) with KCN and anhyd. HCN yields α -hydroxy- β -phenylsuccinonitrile (V), m.p. 89°, which in presence of traces of moisture passes into the corresponding nitrile-amide (II), m.p. 62°. (V) is transformed by conc. HCl at 100° into α -hydroxy- β -phenylsuccinimide, m.p. 177°, which is more sol. in aq. NaOH than in H_2O . Boiling 30% NaOH slowly transforms (V) or (VI) into NH_3 with some HCN and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$. H. W.

Polymembered ring systems. VI. Tendency of formation of polymethylene ketones with more than twenty carbon atoms. K. ZIEGLER and W. HECHELHAMMER (Annalen, 1937, 528, 114—142; cf. A., 1934, 1220).—Nitriles with 20—27, 29, 30, and 34 C are obtained partly from the corresponding dibromides and partly from the dicarboxylic acids and their purity is placed beyond doubt by the regularities of the m.p. in the odd and even series. These are converted into the corresponding cyclic ketones by the process described previously (*loc. cit.*). Reasons are advanced for basing the comparative tendency of ring formation on the yield of crude ketone and, on this basis, there is a feeble periodicity in the region $\text{C}_{20}\text{—C}_{30}$. The form of the m.p. graph of cyclic ketones beyond C_{25} cannot yet be definitely ascertained but uniformity in physical properties, such as would be expected from homologous substances of this mol. magnitude, is not observed. In the relationship between mol. depression of the f.p. and no. of ring members the position of cyclo-dodecanone is exceptional. Thence the mol. depression increases but the difference between neighbouring homologues is small. The subsequent decline is irregular and "odd" and "even" graphs are obtained pointing to a pronounced change in the fine structure of the mols. at about C_{23} .

H esters of dicarboxylic acids with ≥ 12 C are conveniently obtained by heating the acid with MeOH and $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ until the titre does not diminish further or by heating the acid and normal ester with $\text{MeOH}\cdot\text{H}_2\text{O}$ containing $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$. The method is not readily applicable to more complex H esters, which are best obtained by repeated partial hydrolysis of the normal esters. Electrolysis is carried out by Ruzicka's method but with use of a Pt gauze anode. The cyclisation of α -dicyanohexadecane to α -cyanocycloheptadecanone, b.p. 139—141°/0.001 mm., m.p. 43°, and its oxidation to *pentadecane- α -dicarboxylic acid*, m.p. 118° (*Et*₂ ester, m.p. 43°), are described. For the Bouveault-Blanc reduction of esters to glycols the use of synthetic

(not fermentation) BuOH is recommended. This is dehydrated by addition of somewhat > the amount of Na required by the H₂O present, followed by the corresponding quantity of BuOAc, after which the mixture is heated until hydrolysis is complete; after cooling the pptd. NaOAc is removed. The ester in this solvent is added to the Na with brisk stirring at about 70° and the temp. is gradually raised to 140–150°. The glycols are converted into the dibromides by HBr–AcOH at about 100° (1:25-dibromopentacosane, m.p. 63°, b.p. 208°/high vac.) and thence into the nitriles by pure KCN in 90% EtOH (1:25-dicyanopentacosane, m.p. 75.5–76.5°; α,β -dicyanotricosane, m.p. 69°). Interaction of the higher bromides with NaOEt (4 mols.) and CH₂(CO₂Et)₂ (8 mols.) (*Et*₄ tricosane- α,ω,ω -tetracarboxylate, m.p. 49°; *Et*₄ heptacosane-1:1:27:27-tetracarboxylate, m.p. 52°), hydrolysis of the esters, conversion of the acids into nitriles, and cyclisation of the latter are described. The following data appear new: cycloheptacosanone, b.p. 156°/0.2 mm., m.p. 49–50° (semicarbazone, m.p. 49–50°); cyclodocosanone, b.p. 158–160°/0.25 mm., m.p. 41–42° (semicarbazone, m.p. 176–177°); cyclotricosanone, b.p. 158–161°/0.2 mm., m.p. 39–40° (semicarbazone, m.p. 175–176°); cyclotetracosanone, b.p. 186–189°/0.3 mm., m.p. 36–38° (semicarbazone, m.p. 170.5–171.5°); cyclopentacosanone, b.p. 198–199°/0.2 mm., m.p. 37.5–38.5° (semicarbazone, m.p. 170–171°); cyclohexacosanone, b.p. 195–198°/0.3 mm., m.p. 41.5–43° (semicarbazone, m.p. 165–166°); cyclooctacosanone, b.p. 217–219°/0.3 mm., m.p. 49–50° (semicarbazone, m.p. 161°); cyclononacosanone, b.p. 225–227°/0.3 mm., m.p. 45–46° (semicarbazone, m.p. 45–46°); cyclotritriacontanone, b.p. 235–240°/0.2 mm., m.p. 52.5–53.5° (semicarbazone, m.p. 151.5–152.5°). H. W.

γ -Benzoylbutyronitrile [δ -keto- δ -phenyl- γ -valeronitrile]. C. F. H. ALLEN and W. L. BALL (J. Amer. Chem. Soc., 1937, 59, 686–689).—Bz-[CH₂]₃-CO₂Me and NH₃ in aq. EtOH give an unstable compound, Bz-[CH₂]₃-CO-NH₂.NH₃, m.p. 120–121°, which decolorises Br and KMnO₄ and in CCl₄, CHCl₃, C₆H₆, or hot H₂O gives δ -keto- δ -phenyl-valeramide (I), m.p. 144° [2:4-dinitrophenylhydrazones (II), m.p. 195–196°], very readily hydrolysed; long reaction gives a poor yield of (I) and a substance, m.p. 320°, possibly $\begin{pmatrix} \text{NH}\cdot\text{CO}\cdot\text{CH}_2 \\ \text{O}(\text{CH}_2\text{Ph})\cdot\text{CH} \end{pmatrix} > \text{C}$. Hot Ac₂O converts pure (I) into the nitrile (III), b.p. 135–140°, m.p. 38° (dinitrophenylhydrazones, m.p. 173–175°; semicarbazone, m.p. 176–177°), which is readily hydrolysed by acid, but with HBr-CHCl₃ gives (?) the "imide bromide," m.p. 205–210°, and with dry KOAc-EtOAc affords (I). When heated alone or in AcCl, (I) gives 2-keto-6-phenyl-1:2:3:4-tetrahydropyridine, which is also obtained by passing dry NH₃ into (I) at 160–170° and with 2:4-(NO₂)₂C₆H₃-NH-NH₂ yields (II). (I) may be a mixture of the open-chain form with

CH₂< $\begin{pmatrix} \text{OO}\cdot\text{NH} \\ \text{CH}_2\cdot\text{CH}_2 \end{pmatrix}$ >CPh-OH. Br converts (III) into a complex mixture, containing a little 6-phenyl-2-pyridone, probably formed by partial cyclisation of (III) by HBr prior to reaction with Br. 6-Amino-

2-phenylpyridine could not be obtained.

Cl-[CH₂]₃-COPh with KCN or CuCN gives excellent yields of benzoylcyclopropane. R. S. C.

Action of mixed organo-magnesium compounds on phenylhydrazones of ketones. New reaction of organo-magnesium compounds. P. GRAMMATIKAKIS (Compt. rend., 1937, 204, 502–504; cf. A., 1936, 837).—The phenylhydrazones of COPh₂, COPhMe, and COMe₂ with MgEtBr afford, respectively, CPh₂:NPh, α -phenyl- and α -methyl-indole. In each case some of the original ketone, NH₃, and NH₂Ph are formed. Cyclisation is the principal reaction when the structure of the original ketone permits it. J. L. D.

Formation of nitrones by action of aromatic nitroso-compounds on methylene ketones. A. SCHÖNBERG and R. MICHAELIS (J.C.S., 1937, 627–628).—3:3-Diphenyl-1-hydrindone and PhNO or *p*-NMe₂-C₆H₄-NO in warm aq. EtOH-NaOH give, respectively, 3:3-diphenylindanedione-2-anil oxide, m.p. 204°, and -2-*p*-dimethylaminoanil oxide, m.p. 233–234°, both hydrolysed by boiling 45% H₂SO₄ to 3:3-diphenylindanedione, m.p. 152–153°. The mechanism suggested also explains the formation of the dinitrone from diazomethane and PhNO thus: CH₂N₂ + PhNO \rightarrow N₂ + CH₂:NPhO \rightarrow [CH:NPh-OH]₂ + PhNO \rightarrow [CH:NPhO]₂ + NPh-OH. J. W. B.

Pyrene. I. K. DZIEWOŃSKI and L. STERNBACH (Rocz. Chem., 1937, 17, 101–104).—Pyrene and AcCl in PhNO₂ in presence of AlCl₃ at 20° yield methyl 3-pyrenyl ketone, (I), m.p. 94° [oxime (II), m.p. 198°; phenylhydrazone, m.p. 168°; picrate, m.p. 160°]. (II) yields 3-acetamidopyrene, m.p. 260°, by the Beckmann change, whence 3-aminopyrene, m.p. 117°. (I) and S (2 hr. at 230–260°) give bis-4:3-pyrenolthiophenindigo, m.p. >400°. (I) and MeMgI in Et₂O afford 3-isopropenylpyrene, m.p. 61.5–62.5° (picrate, m.p. 146–147.6°). R. T.

Ketimine compounds formed in the micro-detection of magnesium and beryllium.—See A., I, 319.

Relations between chemical properties and "colour" of methoxybenzophenoneoximes and their derivatives. M. MARTYNOFF (Ann. Chim., 1937, [xi], 7, 424–492).—The action of CH₂PhCl and NaOEt on methoxybenzophenoneoximes gives a mixture of O-compounds (I) the constitution of which is established by their synthesis with NH₂·O-CH₂Ph, and N-derivatives (II), the structure of which is based on their hydrolyses by HCl, their reduction by Na and abs. EtOH, and their spectroscopic behaviour, which establish the formula OMe-C₆H₄-CHPh-NO:CHPh. In some cases (II) are hydrolysed by HCl to NH₂·OH owing to previous isomerisation to OMe-C₆H₄-CHPh-O·N:CHPh. (I), like the oximes from which they are derived, are reduced by Na and EtOH to primary amines, fission occurring between O and N. (II) under like conditions afford *sec.* amines with similar form and length of chain. Photochemical stereomutation of (I) resembles that of the parent oximes whereas (II) are rapidly decomposed and resinified by ultra-violet

light. Replacement of H of the functional group of oximes by CH_2Ph causes slight increase in the coeff. of absorption and slight displacement of the bands towards the visible end. The entirely different character of the absorption of (II) proves a profound change of structure. The *syn*- and *anti*-forms of (I) differ from one another somewhat in colour but the differences are small and consist essentially in a displacement of the bands and a variation in the intensity of the absorption without sensible modification in the form of the bands. The methoxybenzophenones are most conveniently obtained by interaction of the requisite methoxybenzoyl chloride with ZnPhBr (obtained from MgPhBr and ZnCl_2 in Et_2O) in PhMe . The prep. of the oximes from the ketones or ketimines is described. The following observations appear new. Labile *o*-methoxybenzophenoneoxime, m.p. 159° in a preheated bath, can be obtained only in cold solution. *o*-Methoxybenzophenoneketimine, m.p. 45° , is obtained from *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ and MgPhBr or from PhCN and *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$. *m*-Methoxybenzophenoneoxime has m.p. 98° ; a labile form could not be isolated. The product, m.p. 116° , appears to be the more stable form of *p*-methoxybenzophenoneoxime; the relative ease of isolation and of interconversion of the two forms indicates a smaller influence of OMe in the *p*- than in the *o*- or *m*-position on the orientation of OH . *o*-Methoxybenzophenoneoxime CH_2Ph ether, m.p. 78° ; *N*-*o*-methoxybenzhydrylbenzaldoxime (VI), m.p. 158.5 — 159.5° , hydrolysed by HCl to PhCHO , *di*-*o*-methoxybenzhydryl ether, m.p. 136 — 137° (obtained also by the action of heat on *o*-methoxybenzhydrol), NH_2OH , and *O*-*o*-methoxybenzhydrylbenzaldoxime, m.p. 85° (reduced by Na and EtOH to $\text{CH}_2\text{Ph}\cdot\text{NH}_2$, identified as $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$); reduction of (III) by Na and EtOH affords benzyl-*o*-methoxybenzhydrylamine (hydrochloride, m.p. about 150 — 155° ; *Ac* derivative, m.p. 121°). *m*-Methoxybenzophenoneoxime CH_2Ph ether, b.p. 214 — 216° / >0.5 mm.; *N*-*m*-methoxybenzhydrylbenzaldoxime, m.p. 113 — 115° , converted by HCl into PhCHO , NH_2OH , and non-cryst. material not volatile without decomp.; *p*-methoxybenzophenoneoxime CH_2Ph ether, m.p. 74° ; *N*-*p*-methoxybenzhydrylbenzaldoxime, m.p. 168° , converted by HCl into PhCHO and material which, when distilled, gives $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-*p*-anisylethane, m.p. 180° . H. W.

Monoximes of aromatic-aliphatic α -diketones. New α -diketones and their dioximes. C. PHILIPP and S. MÜLLER (Annalen, 1937, 528, 296—302).—Oximation of diketones, $\text{COAr}\cdot\text{COAlk}$, in an alkaline or acid medium gives first the β -monoxime (I), $\text{COAr}\cdot\text{CAlk}\cdot\text{N}\cdot\text{OH}$, and further reaction occurs only when this stage has been completed. In acid solution the product invariably contains considerable amounts of (I) as well as dioxime (II). Further oximation of the α -monoxime (III), $\text{OH}\cdot\text{N}\cdot\text{COAr}\cdot\text{CO}\cdot\text{Alk}$, gives (II) exclusively. Treatment of (II) with dil. H_2SO_4 affects the $\alpha\cdot\text{N}\cdot\text{OH}$ first. The conversion of monoxime into diketone by boiling dil. H_2SO_4 proceeds smoothly with (I) though frequently more slowly than with (III). Hydrolysis of (III) is accompanied by partial isomerisation to (I). The following compounds

appear new: acetyl-*p*-toluoyl- β -monoxime, m.p. 116° , and -dioxime, m.p. 226° ; acetyl-*p*-chlorobenzoyl, m.p. 32° (slowly decomp. with formation of $\text{p}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{CO}_2\text{H}$ by hot acids), its β -monoxime, m.p. 113° , and dioxime, m.p. 220° ; acetyl-*p*-ethoxybenzoyl, b.p. $178^\circ/35$ mm. (β -monoxime, m.p. 119° ; dioxime, m.p. 209°). Contrary to Borsche (A., 1907, i, 326), the product of the hydrolysis of acetyl-*p*-anisoyl- α -monoxime is the β -monoxime, not pyruv-*p*-anisidide. H. W.

Transformation of $\alpha\gamma$ -amino-ketones into $\alpha\delta$ -nitro-ketones. B. REICHERT and H. POSEMANN (Arch. Pharm., 1937, 275, 67—83).— MeNO_2 condenses in presence of alkali at the β -C with 1, 2, or 3 mols. of $\alpha\beta$ -unsaturated ketones according to the nature of the ketone. Isolation of vinyl ketones from bases, $\text{COR}\cdot[\text{CH}_2]_2\cdot\text{NMe}_3$, is usually impossible owing to decomp., but when the bases are heated with MeNO_2 and alkali condensation of the "nascent" vinyl ketone gives good yields of the γ -nitro-ketones. Benzylidene-ketones condense in this way, but dibenzylidene-ketones condense with only one mol. of MeNO_2 . The nitro-ketones do not condense with aldehydes, but with isatin, best in presence of NH_3 , give 2-substituted 3- β -nitroethylquinoline-4-carboxylamides. $\text{COPh}\cdot[\text{CH}_2]_2\cdot\text{NMe}_2$, MeNO_2 , and KOH in hot MeOH give γ -nitrobutyrophenone (I), m.p. 66° [semicarbazone, m.p. 163° (decomp.)], hydrolysed by $\text{H}_2\text{C}_2\text{O}_4$ without decomp.; δ -nitro- $\alpha\eta$ -diphenylheptane- $\alpha\eta$ -dione (II), m.p. 133° , and δ -nitro- $\alpha\eta$ -diphenyl- δ - γ' -keto- γ' -phenylpropylheptane- $\alpha\eta$ -dione, m.p. 152° ; under Kohler's conditions (A., 1923, i, 1118) much (I) and some (II) are formed. Allen and Bell's compound, m.p. 132° (A., 1934, 1103), was a mixture. The structure of (I) is proved by reduction, best by Clemmensen's method, to 2-phenylpyrrolidine. (I) and isatin in aq. $\text{MeOH}\cdot\text{NH}_3$ give 2-phenyl-3- β -nitroethylquinoline-4-carboxylamide, m.p. 243 — 244° (decomp.), which cannot be hydrolysed without decomp. $\text{p}\cdot\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_2\text{H}_4\cdot\text{NMe}_2$, MeNO_2 , and NaOMe give 4-methoxy- γ -nitrobutyrophenone, m.p. 69 — 70° [semicarbazone, m.p. 177 — 178° (decomp.)], and thence 2-*p*-anisyl-3- β -nitroethylquinoline-4-carboxylamide, m.p. 217° (cannot be hydrolysed). Similar reactions lead to 3:4-dimethoxy- γ -nitrobutyrophenone, m.p. 95 — 96° [semicarbazone, m.p. 182 — 183° (decomp.)], δ -nitro- $\alpha\eta$ -di-(3:4-dimethoxyphenyl)heptane- $\alpha\eta$ -dione, m.p. 125 — 126° , 2- β -nitroethylcyclohexanone, b.p. $160^\circ/14$ mm. [semicarbazone, m.p. 151 — 152° (decomp.)], and ϵ -nitropentan- β -one (from $\text{COMe}\cdot\text{CH}\cdot\text{CH}_2$), b.p. $115^\circ/12$ mm. [semicarbazone, m.p. 141° (decomp.)]. The appropriately substituted $\text{COMe}\cdot\text{CH}\cdot\text{CHPh}$ give ϵ -nitro-*p*-anisyl (III), m.p. 85 — 86° [semicarbazone, m.p. 176° (decomp.)], -3:4-dimethoxyphenyl-, m.p. 90 — 91° [semicarbazone, m.p. 171 — 172° (decomp.)], and -3:4-methylenedioxyphenyl-pentan- β -one, m.p. 97 — 98° [semicarbazone, m.p. 175 — 176° (decomp.)], and thence by H_2 -Pd or $\text{Zn}\cdot\text{Hg}\cdot\text{HCl}$ 4:3':4'-dimethoxyphenyl- [hydrochloride, m.p. 211 — 212° (decomp.)], and 4-*p*-anisyl-2-methylpyrrolidine (picrate, m.p. 157 — 158°). $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4(\text{OMe})_2\cdot\text{NO}_2$ gives δ -nitro- β -phenyl- α -2-nitro-4:5-dimethoxyphenylbutan- α -one, m.p. 135 — 136° , which with Pd-C in $\text{AcOH}\cdot\text{EtOAc}$ absorbs 3H_2 to give δ -nitro- β -phenyl- α -2-amino-3:5-dimethoxy-

phenylbutan- α -one, m.p. 156—157° (*Ac* derivative, m.p. 158°, hydrolysed by alkali without decomp.; couples with β -C₁₀H₇·OH after diazotisation). CO(CH:CHPh)₂ gives ζ -nitro- α -diphenyl- Δ^{α} -hexen- γ -one, m.p. 118—120°, which gives a *semicarbazone*, m.p. 203°, but is probably enolic since it gives a red FeCl₃ colour and immediately decolorises Br and KMnO₄. CO(CH:CH·C₆H₄·OMe)₂ gives the *keto*-, m.p. 140° (reacts slowly with Br and KMnO₄; no FeCl₃ colour), and *enol*-form, m.p. 120—122° (reacts at once with Br and KMnO₄; red FeCl₃ colour), of ζ -nitro- α -*p*-anisyl- Δ^{α} -hexen- γ -one, the *keto*-form being also obtained from (III) and *p*-OMe·C₆H₄·CHO.

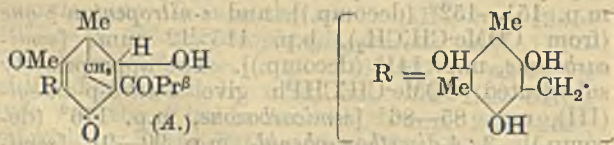
R. S. C.

Condensation of naphthalyl chloride with acetoacetic ester. J. SZUSZKO and B. SZYCH (Rocz. Chem., 1937, 17, 111—117).—Naphthalyl chloride and Et sodioacetoacetate in C₆H₆ at 0° yield Et *perinaphthindandionecarboxylate*, from which a mixture of the free acid and *perinaphthindandione* is obtained by heating in alkaline solution. R. T.

Mixed phenoxyphenyl, diphenyl, and furyl alkyl ketones.—See B., 1937, 328.

Reduction of 2-acylresorcinols. I. Reduction of 2-acetylresorcinol and its dimethyl ether. D. B. LIMAYE and (MISS) I. GHATE (Rasayanam, 1936, 1, 39—42).—2-Acetylresorcinol Me₂ ether (I) is reduced by Na—EtOH to 2 : 6-dimethoxyphenylmethylcarbinol, m.p. 58°, and to 2-ethylresorcinol Me₂ ether (II), m.p. 60°, demethylated (AlCl₃) to 2-ethylresorcinol (III). (III) is also obtained from 2-acetylresorcinol by Clemmensen reduction, which in other experiments gave resorcinol. Clemmensen reduction of (I) in some experiments gave (II), and in others resorcinol Me₂ ether, also obtained by boiling (I) with HCl. 2-Propionylresorcinol, m.p. 139°, yields 2-propylresorcinol, m.p. 100—102°. E. W. W.

Anthelmintics : kouso. I. Protokosin. B. A. HEMS and A. R. TODD (J.C.S., 1937, 562—566).—Protokosin (I), C₂₂H₂₈O₇, m.p. 182°, [α]_D +8·0° in CHCl₃ (amorphous Ac₃ derivative, m.p. 90—100°; contains 1 OMe, 3 OH, 4 C-Me), is isolated in 0·4% yield from the Et₂O extract of dried kouso (*Hagenia abyssinica*) together with kosotoxin (cf. Leichsenring, A., 1894, i, 424), but no trace of kosidin (Lobeck, A., 1902, i, 167) [probably impure (I)] could be detected. When boiled with Zn dust—20% aq.



NaOH (I) affords Pr^sCO₂H (equiv. to 1 Pr^sCO per mol.), *C*-trimethylphloroglucinol, and kosin, separated by fractional crystallisation from MeOH into α - (II), m.p. 158° (Ac₃ derivative, m.p. 123°), and β -kosin (III), m.p. 120° (Ac₃ derivative, m.p. 155°), both of which are isomeric with (I) but contain 2 OMe. Fusion of (I) with KOH at 300° gives *C*-monomethylphloroglucinol, identical with a specimen synthesised by

the method of Curd *et al.* (A., 1933, 609). Other degradation experiments failed to give definite products, but the structure (A) is tentatively suggested for (I), (II) and (III) then being represented by the isomeric forms of (B). J. W. B.

Dehydrogenation of secondary alcohols to ketones. I. Preparation of sterol-ketones and sexual hormones. R. V. OPPENAUER (Rec. trav. chim., 1937, 56, 137—144).—The method consists in the reversal of the method of Meerwein (A., 1925, i, 1239) and Ponndorf (A., 1926, 520) for the reduction of ketones with Al alkoxides. The sterol is refluxed with a considerable excess of COMe₂, C₆H₆, and Al(Obuⁿ)₃, moisture being excluded. In this way cholestenone (I) is obtained from cholesterol (II), *ergostatrienone*, m.p. 131—132·5°, [α]_D −15·7° in CHCl₃ [*semicarbazone*, m.p. 252—254° (decomp.); *Me ether*, m.p. 140—141°, of the *enol*], from ergosterol, androstenedione from dehydroandrosterone, progesterone from pregnenolone, methyltestosterone from 17-methyl- $\Delta^{5,6}$ -androstene-3 : 17-diol, and testosterone acetate from 17-acetyl- $\Delta^{5,6}$ -androstene-3 : 17-diol. Curves are given showing the rate and extent of conversion of (II) into (I) for various initial amounts of (II), COMe₂, and Al(Obuⁿ)₃. H. G. M.

Sterols. VIII. Preparation of androstane-dione from allopregnanediol. R. E. MARKER, O. KAMM, D. M. JONES, and T. S. OAKWOOD. IX. Isolation of *epipregan-3-ol-20-one* from human pregnancy urine. R. E. MARKER, O. KAMM, and R. V. MCGREW. X. Cholesterol derivatives. R. E. MARKER, O. KAMM, G. H. FLEMING, A. H. POPKIN, and E. L. WITTE. XII. Synthetic preparation of *epiallopregnanolone*, the androgenic principle of human pregnancy urine. R. E. MARKER, O. KAMM, D. M. JONES, E. L. WITTE, T. S. OAKWOOD, and H. M. CROOKS. XIII. Dihydroequilenins. R. E. MARKER, O. KAMM, T. S. OAKWOOD, and F. H. TENDICK (J. Amer. Chem. Soc., 1937, 59, 614—616, 616—618, 619—621, 768, 768—769; cf. A., 1936, 1506).—VIII. Progesterone is correlated with androsterone (I) by conversion of *allopregnanedione* into *androstanedione* (II). The former dione, m.p. 199—200°, obtained by CrO₃-oxidation of the mixture of *pregnanediol* and *allopregnanediol* isolated from human urine, with H₂-PtO₂ in AcOH at 3 atm. gives (trans-) *allopregnanediol*, m.p. 195—196°, the *diacetate*, m.p. 142—143°, of which with KOH—MeOH at 15—20° gives the 20-*monoacetate*, m.p. 170—171°. Oxidation of this with cold CrO₃—AcOH gives (trans-) *allopregnan-20-ol-3-one acetate*, m.p. 156°. The derived (trans-) *allopregnan-20-ol-3-one*, m.p. 195°, is dehydrated by ZnCl₂—AcOH and ozonised, yielding (II), m.p. 128° [also obtained with m.p. 132° from (I)], and a *substance*, m.p. 185°.

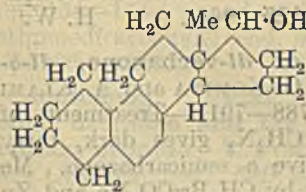
IX. The physiological action of sex hormones is probably accompanied by oxidation and/or reduction. 10,000 gals. of human pregnancy urine yielded no progesterone; it contained mostly *pregnanediol* and *allopregnanediol* and *epiallopregnan-3-ol-20-one* (I) (1—2 mg. per gal.), m.p. 162—164°, [α]_D²⁰ +91° in EtOH (*acetate*, m.p. 139—140°, [α]_D²⁰ +112° in EtOH; stable to Br; not pptd. by digitonin), oxidised by

CrO_3 to *allopregnanedione* and hydrogenated (PtO_2) in AcOH to *trans-epiallopregnane-3:20-diol*, m.p. 205—207° (*diacetate*, m.p. 124°). (I) is the first stage in reduction of progesterone. Urine is freed from theelol and theelin by Doisy's method; carbinols are then removed as Na phthalates; OH-ketones are removed from diols as sol. betainehydrazones; (I) is then purified as *semicarbazone*, m.p. 248—250° (decomp.).

X. Cholesteryl chloride and CrO_3 - AcOH at 55° give a 25% yield of *7-ketocholesteryl chloride* (I), m.p. 145° (*semicarbazone*, m.p. 176°), which with KOH in hot $\text{Bu}^\circ\text{CO}_2\text{H}$ (no reaction in AcOH) gives *7-ketocholesterylene*, m.p. 114° (obtained as sole product by KOH - EtOH), and *epicholesterol*, and with H_2 - PtO_2 in AcOH at 3 atm. affords a little α -cholestyl chloride (II) and *7-hydroxycholestyl chloride* (III), an oil. Crude (III) with $\text{Na-C}_5\text{H}_{11}\text{OH}$ affords *cholestan-7-ol*, m.p. 117.5°, and with CrO_3 gives *7-ketocholestyl chloride*, m.p. 139°. $\text{Al}(\text{OPr}^s)_3$ and (I) give *7-hydroxycholesteryl chloride*, m.p. 142° (*benzoate*, m.p. 119°), hydrogenated (PtO_2 ; 3 atm.) to a mixture of (II) and (III).

XII. *epialloPregnan-3-ol-20-one* (I), new m.p. 170°, is the androgenic principle of human pregnancy urine, being about as active (rat test) as androsterone. It is synthesised thus. By the carbinol degradation *3-chloroallocholanic acid*, m.p. 180°, affords successively its *Me* ester, m.p. 133°, the *diphenylcarbinol*, m.p. 171°, *3-chloroallonorcholanic acid* (*Me* ester, m.p. 178°), the *diphenylcarbinol*, m.p. 183°, *3-chlorobis-norcholanic acid*, m.p. 231° (*Me* ester, m.p. 150°), and the *diphenylcarbinol*, m.p. 146°. The last-mentioned carbinol is dehydrated, ozonised, and treated with KOH . The resulting (I) is purified by means of the H succinate and semicarbazone.

XIII. Equilenin and $\text{Al}(\text{OPr}^s)_3$ give dihydroequilenin, m.p. 215° (*benzoate*, m.p. 204°), and its *epimeride*, m.p. 248° (*diacetate*, m.p. 124°; *benzoate*, m.p. 215°). Hydrogenation (PtO_2) is accompanied by dehydration, giving a 70% yield of a substance (annexed formula), $\text{C}_{18}\text{H}_{24}\text{O}$, m.p. 140° (*acetate*, m.p. 104°). R. S. C.



Synthesis of the female ovarian hormone "folliculosterone." I. A. REMEZOV (*Biochimia*, 1937, 2, 344—366; cf. Marker *et al.*, *A.*, 1936, 1256).—The hormone (I), $\text{C}_{18}\text{H}_{22}\text{O}_2$, m.p. 248.0—248.5°, obtained by oxidation of the side-chain of neoergosterol, is probably 3-hydroxy-17-keto-5:7:9- α -estratriene. 1 mg. of (I) is equiv. to 10,000 international units. W. McC.

Simple preparation of the chloroketone, $\text{C}_{10}\text{H}_{27}\text{OCl}$, dehydroandrosteryl chloride. E. S. WALLIS and E. FERNHOLZ (*J. Amer. Chem. Soc.*, 1937, 59, 764—765).—This chloride, m.p. 154°, $[\alpha]_D^{25} + 14.6^\circ$ in CHCl_3 , is obtained from dehydroandrosterone in 83% yield by PCl_5 in CHCl_3 . R. S. C.

Hormones of the androsterone group. N. D. ZELINSKI and M. I. USCHAKOV (*Bull. Acad. Sci. U.R.S.S.*, 1936, 879—900).—A *semicarbazone*,

$\text{C}_{27}\text{H}_{47}\text{O}_2\text{N}_3$, m.p. 221—223°, yielding a *hydroxyketone* (I), m.p. 175—177°, on hydrolysis, is obtained as a by-product of oxidation of ϵ -cholestanyl acetate. The probable structure of (I) is discussed. Dehydroandrosterone (II) and BzO_2H yield the 5:6-*oxide*, m.p. 228.5°, of (II), from which *androstane-3:5:6-triol-17-one*, m.p. 301—302°, is obtained. R. T.

Separation of hydroxy-compounds of the *cyclopentanopolyhydrophenanthrene* series.—See B., 1937, 393.

Isomerisation of $\Delta^5:6$ -dehydroandrosterone and compounds derived therefrom.—See B., 1937, 393.

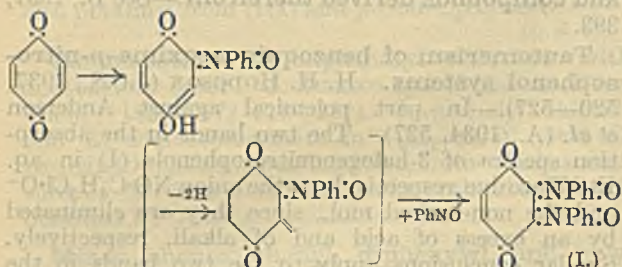
Tautomerism of benzoquinoneoxime-*p*-nitrosophenol systems. H. H. HODGSON (*J.C.S.*, 1937, 520—527).—In part polemical against Anderson *et al.* (*A.*, 1934, 527). The two bands in the absorption spectra of 3-halogenonitrosophenols (I) in aq. EtOH are due, respectively, to the anion $\text{NO}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{O}^-$ and the non-ionised mol., since they are eliminated by an excess of acid and of alkali, respectively. Similar conclusions apply to the two bands in the spectra of 3-halogenbenzoquinone-4-oximes (II) which are due to $\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NO}^-$ and $\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{N}\cdot\text{OH}$, respectively. The differences between the absorption spectra of (I) and (II) are found in the widely different ϵ vals. for the two series. The following data are, respectively, the position of the band peak due to the ion (A.), its ϵ val., the band due to the non-ionised compound, and its ϵ val.: for (I), Cl, 4010, 1875, 2990, 6875; Br, 4015, 5625, 3040, 12,500; I, 4050, 9375, 3080, 12,500; for (II), Cl, 3990, 6875, 3030, 15,000; Br, 4015, 6250, 3040, 8750; I, 4030, 5625, 3080, 7500. Whereas the Cl-compounds of (I) and (II) possess considerable stability in acid and in alkaline solution, the Br- and I-compounds undergo immediate conversion into the more stable quinone monoximes. The *Me* ethers of (I) exhibit single absorption bands at about 3625 A., *i.e.*, between those of the mol. and ion forms of (I); the band of the *Me* ether of (II) is about 3200 A. (ϵ , approx. 12,000). The spectrum of 2-chloro-4-nitrosophenol (III) similarly consists of two bands at 3125 (ϵ , 6250) and 4125 A. (ϵ , 5625), which are suppressed by acids and alkalis, respectively, whereas the band of 2-chloro-4-nitrosoanisole is at 3500, and that of 2-chlorobenzoquinone-4-oxime *Me* ether is at 3300 A. Contrary to Anderson *et al.*, (III) is benzenoid in agreement with the author's earlier conclusion (*A.*, 1932, 734) based on chemical evidence. Correlation between the spectra and electronic strain in the mol. is attempted. J. W. B.

Preparation and constitution of *cyclohexylammonium* 2:5-di(*cyclohexylamino*)-1:4-benzoquinone-3:6-disulphonate, 2:5-di(*cyclohexylamino*)-1:4-benzoquinone, and quinol-2:5-disulphonic acid. (MLLE.) Y. GARREAU (*Compt. rend.*, 1937, 204, 692—694).—Quinol, *cyclohexylamine*, SO_2 , and $\text{Cu}(\text{OH})_2$ (cf. *A.*, 1936, 721), or *cyclohexylammonium* quinol-2:5-disulphonate, *cyclohexylamine*, and CuSO_4 , shaken in air, give *cyclohexylammonium* 2:5-di(*cyclohexylamino*)benzoquinone-3:6-disulphonate. This is hydrolysed by dil. acid to 2:5-di(*cyclohexylamino*)benzoquinone, m.p. 242°,

of which the structure is established by prep. from benzoquinone, or 2:5-dianilinoquinone, and cyclohexylamine. From this, the 2:5-structure of quinol-2:5-disulphonic acid is confirmed.

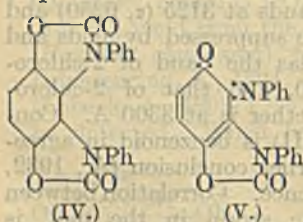
E. W. W.

Action of aromatic nitroso-compounds on quinones. W. GUNDEL and R. PUMMERER (Annalen, 1937, 529, 11—32).—Benzoquinone is slowly converted by PhNO in EtOH at room temp. or, less advantageously, in boiling EtOH-hexane into the corresponding 2:3-dinitrone (I), violent decomp. 179—180°. The course of the change is represented:



Azoxybenzene is also produced in considerable quantity. (I) and Br in AcOH yield the dibromide. (I) is smoothly hydrogenated (Pt-sponge in C_6H_6) to 2:3-dianilinoquinol (II), m.p. 143—144° (decomp.), converted by Ac_2O at room temp. into the NN'- Ac_2 derivative, m.p. (indef.) 236—240° after darkening, and by exhaustive acetylation into the very unstable benziminazolium base [unstable acetate (III), m.p. 135—136° (decomp.); picrate, m.p. 207°; sparingly sol. perchlorate, m.p. 259°]. Conversion into the stable ψ -base, $(OAc)_2C_6H_2<\begin{smallmatrix} NPh \\ NPh \end{smallmatrix}>CMe\cdot OH$, m.p.

142—143°, is best effected by keeping (III) in contact with warm Et_2O . Treatment of (II) with $COCl_2$ in C_6H_6 -PhMe containing $NPhMe_2$ at 100° gives the colourless, stable NN'-diphenylbenzodioxazalone (IV), sublimates at >300°; the anilinohydroxy-N-phenylbenzodioxazalone produced in small amount is oxidised by $FeCl_3$ to the carmine-red o-quinonephenylimine (V), m.p. 254—255°. Both compounds give PhNC when boiled with aq. alkali.



Hydrogenation of (II) in presence of feebly active Pt sponge affords 2-anilino-3-phenylhydroxyaminoquinol, which loses H_2O at 110° and forms 2:3-dianilino-p-benzoquinone, also obtained by oxidising (III) in Et_2O with PbO_2 ; it is transformed by NH_2Ph in EtOH containing AcOH into 2:3:5-trianilino-p-benzoquinone, which, like similar compounds obtained from other aromatic bases, dyes wool in clear yellow shades from a hyposulphite vat. p-Benzo- and tolu-quinone are transformed by p- $NO\cdot C_6H_4\cdot NMe_2$ into the corresponding dinitrones. The dinitrones, $C_{22}H_{20}O_4N_4Cl_2$ (+ $1C_6H_6$ or +0.5 $CHCl_3$), violent decomp. 180—183°, and $C_{26}H_{24}O_4N_4$ are derived from 2:3-dichloro-p-benzoquinone and 1:4-naphthaquinone, respectively, whereas 1:2-naphthaquinone gives the mononitron, $C_{18}H_{16}O_3N_2$, decomp. 180—200°.

H. W.

Spectrochemical study of colours derived from quinoneimine.—See A., I, 217.

Action of hydroxylamine on quinizarin and its derivatives in alkaline medium. C. MAR-SCHALK (Bull. Soc. chim., 1937, [v], 4, 629—636).—When heated with aq. NH_2OH quinizarin affords 2-amino-1:4-dihydroxyanthraquinone (I), m.p. 313—314°, identical with a specimen obtained by reduction of the NO_2 -compound with $(NH_4)_2S$. Similarly Na quinizarin-2-sulphonate affords 3-amino-1:4-dihydroxyanthraquinone-2-sulphonate, and Na 1:4-dihydroxyanthraquinone-2:3-dicarboxylate is converted into 2-amino-1:4-dihydroxyanthraquinone-3-carboxylic acid. The formation of these products probably involves addition of NH_2OH to the quinizarin 2:3-double linking followed by an intramol. reduction, since alizarin and 2-hydroxyanthraquinone with NH_2OH give products from which the original components are regenerated by hydrolysis with 20% HCl at 250°. (I) is converted by glycerol- H_2SO_4 - $PhNO_2$ into 2:3-pyridino-1:4-dihydroxyanthraquinone from which acid browns may be obtained by condensation with aromatic amines in presence of H_3BO_3 and sulphonation of the resulting NH_2 -compounds.

J. W. B.

Manufacture of [higher] alkoxyanthraquinones.—See B., 1937, 328.

Manufacture of 2-aminoquinazarin and substitution products thereof.—See B., 1937, 328.

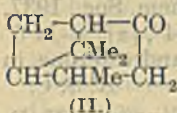
Investigation of catalytic racemisation with deuterium as indicator. H. ERLNMEYER, H. SCHENKEL and A. EPRECHT (Helv. Chim. Acta, 1937, 20, 367—368; cf. this vol., 18).—Catalytic racemisation of l-menthyl d-phenylbromoacetate by KOEt in EtOD gives a product containing D and thus supports the scheme of racemisation advanced by McKenzie (J.C.S., 1924, 125, 1066).

H. W.

Complete synthesis of dl-verbanone, dl-8-pinene, and dl-pinane. G. KOMPPA and A. KLAMI (Ber., 1937, 70, [B], 788—791).—Treatment of pinononyl chloride with CH_2N_2 gives dark, tarry matter which does not give a semicarbazone. Me pinonate is transformed by $CH_2Br\cdot CO_2Me$ and Zn filings in C_6H_6 into Me_2 hydroxyisohomopinocamporate, $CO_2Me\cdot CH<\begin{smallmatrix} CH_2 \\ CMe_2 \end{smallmatrix}>CH\cdot CMe(OH)\cdot CH_2\cdot CO_2Me$, b.p. 170—175°/11 mm., dehydrated by $SOCl_2$ and then hydrolysed to dehydroisohomopinocamporic acid (I), m.p. 194°, which is oxidised by $KMnO_4$ to dl-pinononic acid. (I) is reduced (PtO_2 in AcOH) to isohomopinocamporic acid



(indef.) 120—135°, the Pb salt of which passes at 280—300° into dl-verbanone (II) (semicarbazone, m.p. 218°), identical with that obtained by hydrogenation (PtO_2 in EtOH) of dl-verbenone. Removal of H_2O from dl-verbanol by $SOCl_2$ in C_5H_5N gives dl-8-pinene, b.p. 157—159°/771 mm., oxidised by alkaline $KMnO_4$ to dl-pinocamporic acid, m.p. 185—186°.



H. W.

Structure of isoborneol. I. New isomeride of borneol. V. N. KRESTINSKI and A. ESCHTSCHENKO. II. Velocity of esterification of isomeric dicyclic alcohols of the camphor, camphene, and fenchyl series. V. N. KRESTINSKI, M. NEMILOV, and I. BARDISCHEV (J. Gen. Chem. Russ., 1937, 7, 415—422, 423—429).—I. Achmatowicz's results (A., 1927, 250; 1928, 645) are confirmed.

II. The velocity coeffs. of acetylation of borneol, endoborneol, and fenchyl and isofenchyl alcohol are of the same order of magnitude (0.0111—0.0117), and differ from those of isoborneol, camphene hydrate, and methylcamphenilol (0.00767—0.00779); it is concluded that the members of the respective groups have the same general structure. R. T.

Preparation of bornyl chloride. E. N. ROSTOVSKI and V. SCHEREMETeva (Plast. Massui, 1935, No. 3, 33—34).—Pinene is saturated with HCl at 90°.

CH. ABS. (r)

Totarol. I. W. F. SHORT and H. STROMBERG (J.C.S., 1937, 516—520).—Totarol (I), $C_{20}H_{30}O$, m.p. 132°, $[\alpha]_D^{20} + 41.34^\circ$ in EtOH, gives a *formate*, m.p. 125.5°, *acetate*, m.p. 121.5°, $[\alpha]_D^{18} + 44.58^\circ$ in Et₂O, *H phthalate*, m.p. 161—163°, and *Me ether*, m.p. 92—92.5°, $[\alpha]_D^{18} + 41.95^\circ$ in Et₂O. H₂—Pd reduces (I) with difficulty to *totarane* (II), m.p. 74.5—75°, $[\alpha]_D^{20} - 31.06^\circ$ in Et₂O, and *dihydrototarol*, m.p. 151—151.5°, $[\alpha]_D^{20} + 20.13^\circ$ in Et₂O (*formate*, m.p. 104.5—105°), which is further reduced to *tetrahydrototarol*, m.p. 134.5°. Dehydrogenation of (I) with Se or Pd—C affords C₃H₈ and 7-hydroxy-1-methylphenanthrene, m.p. 190—191°, which forms a *Me ether*, m.p. 133.5—134.5°, and an *acetate*, m.p. 133.5—136°, oxidised to a *quinone*, m.p. 207° (decomp.) [*quinoxaline*, m.p. 244.5—245.5°; corresponding *OH-quinone*, m.p. 228° (decomp.)]. Pd—C dehydrogenates (II) to a *hydrocarbon*, C₁₈H₁₈, m.p. 101.5—102° (*picrate*, m.p. 142.5°), oxidised with CrO₃ to a *quinone*, m.p. 160.5—161.5° (*quinoxaline*, m.p. 154—154.5°), and with K₃Fe(CN)₆ to a phenanthrenedicarboxylic acid, m.p. 200—206° (Me ester, m.p. 135.5—136°). F. R. S.

Caoutchouc. XVIII. The various caoutchouc ozonides and the existence of Harries' primary ozonide. R. PUMMERER and H. RICHTZENHAIN (Annalen, 1937, 529, 33—67).—Examination of various compounds which appear to indicate a relative stability of primary ozonides as defined by Harries gives no confirmation of their existence. It is therefore unnecessary to draw a distinction between ozonides and isoozonides. Isolable ozonides do not contain the Harries ring system, $\begin{array}{c} \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{O} - \text{O} - \text{O} \end{array}$, but the

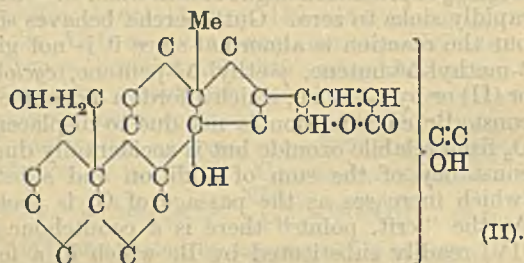
arrangement $\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}$ proposed by Staudinger for isoozonides. The formation of polymeric ozonides is best explained by Staudinger's assumption of the primary formation of "molozonides," which are regarded as a very unstable, intermediate phase. The action of heat on mesityl oxide ozonide (I) gives only COMe₂ and its peroxide, AcCHO, AcOH, and HCO₂H; unchanged mesityl oxide (II) could not be detected with 2:4-(NO₂)₂C₆H₃·NH·NH₂. Cautious reduction of (I) with quinol, NHPh·NHPh, Al—Hg, or Zn dust + AgNO₃ does not appear to give α-acetyl-β-methyl-

M (A., II.)

propane-α,β-diol, which can readily be identified by conversion in 17% H₂SO₄ into the 2:4-dinitrophenylhydrazones, m.p. 164—166° (decomp.). (An apparatus for the reduction of an ozonide immediately after its formation is described.) Fumaric acid does not appear to react with O₃ in EtOAc at —70° and the "acid recovered from the ozonide" by Harries was probably unattacked material. Et₂ fumarate in CCl₄ yields the *ozonide*, m.p. 42—43°, which does not reform the ester when preserved; when obtained in EtOAc at —55° and immediately reduced by Al—Hg it yields only CHO·CO₂Et without sign of a molozonide convertible into Et₂ tartrate. Ozonisation of dihydrodicyclopentadiene in EtOAc at —75° gives an *ozonide*, m.p. 60—62°, which, unlike Staudinger's product, m.p. 125—130°, obtained in CCl₄, is readily sol. in Et₂O; it is scarcely affected by H₂—Pt—SiO₂ at 0° or 20° and liberates I very slowly from HI. More drastic fission by Zn and AcOH leads normally to 3:6-endomethylenehexahydrohomophthalaldehyde, b.p. 112°/0.3 mm. [*di*-2:4-dinitrophenylhydrazones, m.p. 212° (decomp.); (?) *disemicarbazone*, m.p. 189°], which becomes polymerised when preserved. Titration of solutions of caoutchouc (III) with Br during ozonisation indicates a constancy of Br absorption until O₃ is present in slight excess when the absorption rapidly sinks to zero. Guttapercha behaves similarly but the reaction is abnormal since it is not given by β-methyl-Δ^β-butene, γ-ethyl-Δ^β-pentene, cyclohexene, or (II) or by β-ionone, which affords a dioxonide. The const. Br consumption is not due to displacement of O₃ from a labile ozonide but is accidentally due to the constancy of the sum of addition and substitution (which increases as the passage of O₃ is prolonged). At the "crit. point" there is a caoutchouc *ozonide* (IV) readily substituted by Br which in a few min. passes into a *compound* (V) stable to Br. The latter material gives β-bromo- and some β,δ-dibromolävulic acid when reduced with SO₂. Pyridine dibromide hydrobromide is preferable to Br for the titration of (III). Caoutchouc oxide (V), from (III) and BzO₂H, is stable to Br and mixtures of (III) and (VI) in CHCl₃ behave normally with Br until the double linkings are saturated. (IV) and (V) are (C₆H₃O₃)_n and do not differ appreciably from one another in physical and chemical properties except with regard to behaviour towards Br; (V) is stable whereas (IV) absorbs varying amounts of Br reaching 91% of that required by the parent (III). In CHCl₃ (IV) appears to remain unchanged during 14 days at 0° whereas (V) gives rise to lävulic acid peroxide. Attempts to transform (IV) into a polyglycol [·CH₂·CMe(OH)·CH(OH)·CH₂·]_n by cautious reduction with Al—Hg were unsuccessful. Among other reagents, only BzO₂H resembles O₃ in its action towards the sensitiveness of (IV) to Br. Similarly it restricts the bromination of COMe₂ and CH₃Ac·CO₂Et. It appears therefore that the final quantities of O₃ are adequate to produce so much caoutchouc ozonide per acid as is necessary to inhibit substitution by Br; inhibition is most probably due to destruction of HBr. In presence of HBr, COMe₂ immediately decolorises Br, much less rapidly in its absence. BzO₂H in indifferent media oxidises HBr to Br immediately. Passage of O₃ through (III) in CCl₄

causes spontaneous separation of a new *ozonide* (VI) which softens at 85° and is more sparingly sol. in the usual media than that obtained in CHCl_3 . When a deficiency of O_3 is employed essentially (VI) is produced whilst some (III) remains unchanged. The mol. wt. of (VI) in CHBr_3 agrees with $(\text{C}_5\text{H}_8\text{O}_3)_5$ but other properties suggest that it is degraded in this solvent. (VI) has little activity towards HI or Br. H. W.

Toad poisons. Chemical constitution of *marinobufagin*, *cinobufagin*, and *gamabufagin*. H. JENSEN (J. Amer. Chem. Soc., 1937, 59, 767—768).—*Cinobufagin* (I) and Se give the Diels hydrocarbon, $\text{C}_{18}\text{H}_{16}$. *Marinobufagin* (II) and (I) contain 3 ethylenic linkings, since hydrogenation affords α -, m.p. 212—213°, and β -*hexahydromarinobufagin*, m.p. 225—227°, and α -, m.p. 230—232°, and β -*hexahydrocinobufagin*, m.p. 210—212°, with small amounts of acids. Ozonisation of (I) or (II) gives HCO_2H , $\text{CHO}\cdot\text{CO}_2\text{H}$, and $\text{H}_2\text{C}_2\text{O}_4$. (I) and *gamabufagin* (III) contain $\text{CH}_2\cdot\text{OH}$ attached to C_{10} or C_{13} (corresponding to the *ang.*-Me of the sterols), which is eliminated as CH_2O by strong acids or alkalis and is oxidised to CHO by CrO_3 . Acid removes 2 OH as H_2O from (II) and 1 OH from (III). The following structure is suggested for (II); (I) and (III) are probably



similar. The formula $\text{C}_{24}\text{H}_{34}\text{O}_5$ for (III) is confirmed. (III) has only two ethylenic linkings, both in the lactone ring. R. S. C.

Manufacture of hydroxy[coumaran]carboxylic acids and of amides derived therefrom.—See B., 1937, 421.

Geometrical inversion in acids derived from coumarins. IV. Behaviour of the ethers of *cis*- and *trans*-acids. S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1937, 5, A, 249—256).—The interconversion of the *cis*- and *trans*-acids (improved preps.) from coumarin, 7-methyl- and 6-nitro-coumarin with HCl - EtOH , H_2SO_4 , and HgO in neutral, acidic, and alkaline media shows the *trans*-form to be favoured. With conc. H_2SO_4 , hydrolysis of the ether and ring-closure take place. The following are described: 4-methylcoumarinic acid *Me ether*, m.p. 160—161°, from 7-methylcoumarin in MeOH with MeI and NaOMe , and 4-methylcoumaric acid *Me ether*, m.p. 209—210°, from the OH-acid and Me_2SO_4 . J. D. R.

Natural coumarins. XXV. *Fraxinol*, a new component of ash bark. E. SPÄTH and Z. JERZMANOWSKA-SIENKIEWICZOWA (Ber., 1937, 70, [B], 698—702).—Extraction of the (necessarily) fresh bark of *Fraxinus excelsior*, L., with Et_2O and treatment of the extracts with MeOH and H_2O followed

by hydrolysis affords *fraxinol* [6-hydroxy-5:7-dimethoxycoumarin] (I), m.p. 171—172° [*Ac* derivative (II), m.p. 140—141°; *Me ether*, b.p. 160°/0.1 mm., m.p. 76—77°]. 2:6-Dimethoxy-*p*-benzoquinone, m.p. 255° (decomp.), is reduced by SnCl_2 and HCl to 2:6-dimethoxyquinol, m.p. 166—167° (vac.), converted by $\text{Zn}(\text{CN})_2$ and HCl in Et_2O into 3:6-dihydroxy-2:4-dimethoxybenzaldehyde, m.p. 141—142° (vac.). This is transformed by anhyd. NaOAc and Ac_2O into (II), hydrolysed to (I), identical with the natural product. H. W.

Natural coumarins. XXVI. Constitution and synthesis of *ayapin*. E. SPÄTH, P. K. BOSE, and J. SCHLÄGER (Ber., 1937, 70, [B], 702—704).—Exhaustive extraction of the dried leaves of *Eupatorium Ayapana*, Vent., with light petroleum of low b.p. and treatment of the dry extract with boiling H_2O followed by Et_2O leads to *ayapanin*, m.p. 119° (J.C.S., 1910, 97, 1131), and *ayapin* [6:7-methylenedioxy-coumarin] (I), m.p. 231—232° (vac.). (I) is hydrolysed by H_2SO_4 and phloroglucinol to *asculetin* (II) (identified as the Me_2 ether) and obtained synthetically from (II), CH_2I_2 , and NaOMe in MeOH . H. W.

Syntheses in the 5-hydroxybenzopyrone group. II. 5-Hydroxy-4-methylcoumarin. D. B. LIMAYE and G. R. KELKAR (Rasāyanam, 1936, 1, 45—48; cf. this vol., 257).—The substance, m.p. 263°, obtained in poor yield with chromones from 2-acetylresorcinol and Ac_2O - NaOAc (A., 1935, 854) is 5-hydroxy-4-methylcoumarin (*Ac* derivative, m.p. 114°; no FeCl_3 colour), since it or its *Me ether* (I), m.p. 143°, when boiled with N - NaOH and then shaken with Me_2SO_4 , gives 2:6-dimethoxy- β -methylcinnamic acid, m.p. 185°. Hydrolysis without subsequent methylation gives a very poor yield of 2:6-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, but the (OMe) $_2$ -acid could not be obtained from (I) owing to instantaneous ring-closure. R. S. C.

Synthesis of 6-hydroxy-7-acylcoumarones. I. 6-Hydroxy-7-acetyl-3-methylcoumarone. D. B. LIMAYE and N. R. SATHE (Rasāyanam, 1936, 1, 48—59).—Hydrolysis of 3-bromo-7-hydroxy-8-acetyl-4-methylcoumarin (I), m.p. 218° (*semicarbazone*, m.p. >275°; *Ac* derivative, m.p. 226°, degraded by hot alkali), obtained from 8-acetyl-4-methylumbelliferone by Br - AcOH , is abnormal, but its structure is proved by normal hydrolysis of its *Me ether*, m.p. 187°, by $2N$ - NaOH to 7-acetyl-6-methoxy-3-methylcoumarilic acid, m.p. 234° (decomp.), which above the m.p. affords CO_2 and 7-acetyl-6-methoxy-3-methylcoumarone (II), m.p. 75° (*semicarbazone*, m.p. 206°). With hot N - NaOH (I) gives 6-hydroxy-7-acetyl-3-methylcoumarilic acid (III), m.p. 252° (decomp.) [obtained as sole product by $10N$ - NaOH ; mixed *anhydride* with AcOH , m.p. 87°; *Et*, m.p. 103°, and *Me ester*, m.p. 156° (*Me ether*, m.p. 132°); with Me_2SO_4 gives (II); *Bz* derivative, m.p. 113°], 6-hydroxy-7-acetyl-3-methylcoumarone (IV), m.p. 112°, b.p. 290—292° [formed from (III) by loss of CO_2 and also obtained from (I) and hot 7% Na_2CO_3 or from (II) by AlCl_3 ; *semicarbazone*, m.p. 227° (decomp.)], and a substance (V), $\text{C}_{11}\text{H}_{10}\text{O}_3$, m.p. 99°; with hot $3N$ - NaOH it gives an acid, $\text{C}_{12}\text{H}_{10}\text{O}_5$, m.p.

143° (decomp.) (*Me* ester, m.p. 88°; *Me* ether, m.p. 150°; *semicarbazone*), which gives CO₂ and (IV). Ac₂O-NaOAc converts (III) at 160–165° into 6-hydroxy-3-methylcoumarone, m.p. 103°, the *acetate*, m.p. 58°, of which with AlCl₃ at 120–130° gives (IV) and a *substance*, m.p. 190°. Under other conditions (not detailed) (I) gives a *phenol*, m.p. 91°, converted by dehydration into a *substance*, m.p. 120°, both of which with hot acid give (V). R. S. C.

Constitution of nitro-β-methylumbelliferone methyl ether and of chlororesorcinol. D. CHAKRAVARTI and B. C. BANERJI (J. Indian Chem. Soc., 1937, 14, 37–38).—The isomeride of 8-nitro-7-methoxy-4-methylcoumarin, also formed during the nitration of β-methylumbelliferone *Me* ether, is identified as 6-nitro-7-methoxy-4-methylcoumarin (I), m.p. 281°, since it is demethylated to 6-nitro-7-hydroxy-4-methylcoumarin, m.p. 253°, also obtained, m.p. 255°, by condensation of 4-nitroresorcinol with CH₃Ac·CO₂Et. (I) is converted, through the 6-NH₂-compound, into 6-chloro-7-methoxy-4-methylcoumarin, m.p. 252°, also obtained from the 7-OH-compound (A., 1935, 1504) derived from 4-chlororesorcinol, the structure of which (cf. A., 1936, 858) is thus confirmed. E. W. W.

Effect of methylation on the course of hydrolysis of 8-acetyl-4-methylumbelliferone by caustic alkali. Formation of stable *cis*- and *trans*-2-hydroxy-4-methoxy-3-acetyl-β-methylcinnamic acids. D. B. LIMAYE and N. R. SATHE (Rasayanam, 1936, 1, 30–38).—8-Acetyl-4-methylumbelliferone (I) (A., 1932, 521) with Me₂SO₄-NaOH gives 7-methoxy-8-acetyl-4-methylcoumarin, m.p. 137° (*semicarbazone*, m.p. 254°), which with boiling *N*-NaOH gives *cis*-2-hydroxy-4-methoxy-3-acetyl-β-methylcinnamic acid (II), m.p. 163° (decomp.), readily reconverted into (I). (II) is methylated to *cis*-2:4-dimethoxy-3-acetyl-β-methylcinnamic acid (III), m.p. 157–158°, and its *Me* ester, m.p. 95–97°. As a by-product with (II), 2-hydroxy-6-methoxy-3-isopropenylacetophenone (IV), m.p. 61°, is formed, converted by dil. acids into a *substance*, m.p. 204°. With Me₂SO₄, (IV) yields the 2:6-dimethoxy-compound, b.p. 279–280° (*semicarbazone*, m.p. 168°), also obtained from (III) at 200°. A further by-product with (II) is *trans*-2-hydroxy-4-methoxy-3-acetyl-β-methylcinnamic acid (V), m.p. 175° [converted above its m.p. into (IV)], which with Me₂SO₄ gives the 2:4-dimethoxy-acid, m.p. 132°, without ester. (I) with NaOEt-EtOH, followed by HCl, gives (V), also obtained from (II) or (III) and aq. NaOH. E. W. W.

Reactivity of the double linking in coumarins and related αβ-unsaturated carbonyl compounds.

III. Action of mercuric acetate on coumarinic and coumaric acids and esters. P. S. RAO and T. R. SESHADRI (Proc. Indian Acad. Sci., 1936, 4, A, 630–638; cf. A., 1936, 997, 1516).—Coumarinic acid with Hg(OAc)₂-H₂O gives 3:5:α-triacetoxymercuri-β-acetoxymelilotic acid, decomp. at 245° (cf. Naik *et al.*, A., 1934, 1107), which with NaOH-H₂O gives 3:5-diacetoxymercuricoumaric acid (cf. A., 1930, 913). 5-Nitrocoumarinic acid gives 5-nitro-α-acetoxymercuri-β-acetoxymelilotic acid, decomp. at 170°, converted by NaOH-H₂O into 5-nitro-

coumaric acid (I) (cf. *loc. cit.*). Coumaric acid (II) when refluxed with Hg(OAc)₂-MeOH gives 3:5:α-triacetoxymercuri-β-methoxymelilotic acid, m.p. 234° (decomp.) [*Me* ester (III), decomp. at 265°, obtained similarly from the *Me* ester of (II)], converted by H₂S in NaOH into β-methoxymelilotic acid, and by successive treatment with Br-AcOH and KOH-EtOH into 4:6-dibromocoumarilic acid, obtained likewise from (III). By similar methods (I) yields 5-nitro-3:α-diacetoxymercuri-β-methoxymelilotic acid, turns grey at 258° (*Me* ester, decomp. at 238°), converted into (I) by H₂S in NaOH and into 6-bromo-4-nitrocoumarilic acid, m.p. 252–253°, by successive treatment with Br-AcOH and KOH-H₂O, and 4-methylcoumaric acid yields 3:5:α-triacetoxymercuri-4-methyl-β-methoxymelilotic acid, m.p. 228° (decomp.) (*Me* ester, m.p. about 284°), converted by bromination and subsequent treatment with KOH-H₂O into 4:6-dibromo-5-methylcoumarilic acid, m.p. 270°. The coumarilic acids were also obtained from the appropriate bromocoumarins. H. G. M.

Reaction between quinones and sodium enolates. V. 2:3-Dimethylnaphthoquinone and sodiomalonic ester. L. E. SMITH and (Miss) I. M. WEBSTER. VI. Duroquinone and sodioacetoacetic ester. L. E. SMITH and D. TENENBAUM. VII. Bromo-*p*-cunoquinone and sodiomalonic ester. L. E. SMITH and K. C. JOHNSON (J. Amer. Chem. Soc., 1937, 59, 662–667, 667–672, 673–679; cf. A., 1936, 732).—V. 2:3-Dimethyl-1:4-naphthoquinone (I) (modified prep.) and CHNa(CO₂Et)₂ in Et₂O-EtOH, best when stirred in air, give a Na compound, which with HCl gives 6-hydroxy-3-carbethoxy-5-methyl-α-naphthocoumarin (II), m.p. 212–213°, the structure of which is proved by the reactions given below. Thus (I) reacts in the same way as does duroquinone. The yellow colour of the derivatives of (II) makes it unnecessary to postulate a special formula to account for colours of coumarin derivatives. With H₂-Pd in EtOH or MeOH at about 1.2 atm. (II) gives 6-hydroxy-3-carbethoxy-5-methyl-3:4-dihydro-α-naphthocoumarin (III), m.p. 175–176° (*Ac* derivative, m.p. 145–145.5°). Hydrolysis of (II) by most reagents causes decomp., but HCl in aq. COMe₂ gives 6-hydroxy-3-carboxy-5-methyl-α-naphthocoumarin (IV), m.p. 275–276° (decomp.; bath preheated to 240°), 263° (decomp.; no preheating) [*Ac* derivative, m.p. 258° (decomp.)], gives oils when hydrogenated, hydrogenation of which gives mixtures of the carboxy-dihydrocoumarin and decarboxylated dihydrocoumarin, which could not be isolated owing to the ease of oxidation; hydrolysis of (III) gives small amounts of a substance, m.p. 155–159°, probably the corresponding acid, and a substance, m.p. 120–125°, probably 6-hydroxy-5-methyl-α-naphthocoumarin. (II), its yellow *Ac* derivative, m.p. 195–196°, or (IV) with Me₂SO₄-KOH in hot aq. MeOH gives 3-carboxy-6-methoxy-5-methyl-α-naphthocoumarin (V), m.p. 222–225°, also obtained by other methods; under restricted conditions, (II), NaOMe, and Me₂SO₄ give 3-carbethoxy-6-methoxy-5-methyl-α-naphthocoumarin, m.p. 182–183°, also obtained impure when the Na derivative from the original condensation is heated with MeI

in MeOH; with 10% KOH it gives the mono-ether (V). (II) and CH_2N_2 give a substance, m.p. 138—139°. Reduction of (I) by Zn dust leads to 1:4-diacetoxy-2:3-dimethylnaphthalene, m.p. 189—190°, or the unstable quinhydrone, m.p. 139—144° (also obtained in the coumarin condensation in absence of O_2). 2:1:4- $\text{C}_{10}\text{H}_5\text{Me}(\text{OAc})_2$, m.p. 112.5—114°, is obtained from 2-methyl-1:4-naphthoquinone, but neither the free quinol nor its Me_2 ether could be obtained; the quinhydrone (prep. by Pd-hydrogenation in dry Et_2O at 1.34 atm.) with HCl and $\text{Zn}(\text{CN})_2$ in Et_2O gives 64% of 1:4-dihydroxy-3-methyl-2-naphthaldehyde, m.p. 158—160°, which with $\text{CH}_2(\text{CO}_2\text{Et})_2$ and piperidine in EtOH gives (II) and in AcOH the Ac derivative of (II) and with $\text{CH}_2(\text{CO}_2\text{H})_2$ and piperidine in MeOH gives (IV).

VI. Duroquinone reacts with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ in C_6H_6 as with $\text{CHNa}(\text{CO}_2\text{Et})_2$, yielding 0.5 mol. of the quinol and 0.5 mol. of a Na compound, which with HCl affords 6-hydroxy-3-acetyl-5:7:8-trimethylcoumarin (I), m.p. 227—228° (Bz derivative, m.p. 162—163°), the structure of which is proved by the reactions given below. Hydrogenation (Pd; EtOH; 3 atm.) of (I) gives 6-hydroxy-3-acetyl-5:7:8-trimethyl-3:4-dihydrocoumarin, m.p. 164—165° {Ac derivative, m.p. 124—125°, and Me ether (II), m.p. 112—113.5° [oxime, m.p. 156—157° (decomp.)]}, also obtained by hydrogenation of the Ac derivative, m.p. 201—202.5°, and Me ether (III) (prep. only from the solid Na derivative and Me_2SO_4 in MeOH, m.p. 158.5—159.5°; benzylidene derivative, m.p. 187—189°), of (I); oxime, m.p. 179—180° (decomp.)}. Dimethoxyduraldehyde and $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ in MeOH give Et 2:5-dimethoxy-3:4:6-trimethylbenzylidenemalonic acid, an oil, from which (I) is obtained by boiling first with 10% KOH-EtOH and then with HI. Oxidation of (I) or (III) usually causes degradation, but the Na derivative of (I) with Br gives CHBr_3 and a little 6-hydroxy-3-carboxy-5:7:8-trimethylcoumarin. The oxime, m.p. 258—260° (decomp.), of (I) did not undergo Beckmann rearrangement without decomp., but the oxime, m.p. 225—227° (decomp.), of (III) with PhSO_2Cl in $\text{C}_5\text{H}_5\text{N}$ at room temp. gives 3-acetamido-6-methoxy-5:7:8-trimethylcoumarin, m.p. 237—238°, hydrolysed by 6N-HCl to the amine, m.p. 150—151°. 3-Carboxy-6-methoxy-5:7:8-trimethylcoumarin gives (a) the methylamide, m.p. 214—215°, (b) the azide, m.p. about 210° (violent decomp.), which could not be degraded by acid, and (c) a hydroxamic acid, m.p. 236—237°, unchanged by $\text{Ac}_2\text{O}\cdot\text{COMe}_2$.

VII. In accordance with an electronic interpretation bromo- ψ -cumoquinone (I) reacts with $\text{CHNa}(\text{CO}_2\text{Et})_2$ in Et_2O , EtOH, or, less well, C_6H_6 , by 1:4-addition to give a Na compound, decomposed by acid to 8-bromo-6-hydroxy-3-carbethoxy-5:7-dimethylcoumarin (II), m.p. 200°, the structure of which is proved by the reactions described below and by synthesis of derivatives. 5-Bromo- ψ -cumene in CHCl_3 with $\text{H}_2\text{SO}_4\text{--HNO}_3$ (d 1.5) gives the 3:6- $(\text{NO}_2)_2$ -derivative (93% yield), new m.p. 221—222°, reduced (SnCl_2) to 5-bromo-3:6-diamino- ψ -cumene, m.p. 155° (decomp. from 150°), the stannichloride of which with FeCl_3 affords (I), m.p. 79—80° (quinhydrone, m.p. 148.5—149.5°), reduced by SnCl_2 to

bromotrimethylquinol, m.p. 185° (decomp. from 170°) (Me_2 ether, m.p. 71—72°; Ac_2 , m.p. 178—179°, and Bz₂ derivative, m.p. 253—255°). (II) (Ac derivative, m.p. 160—161°) with HCl gives 8-bromo-6-hydroxy-3-carboxy-5:7-dimethylcoumarin (III), m.p. 250° [Ac derivative, (IV), m.p. 223°; Me ether, m.p. 210°, obtained by KOH-MeOH- Me_2SO_4 from (II), (III), or (IV)], and is debrominated by H_2 -Pd in EtOH at 2.8 atm. to yield 6-hydroxy-3-carbethoxy-5:7-dimethyl-3:4-dihydrocoumarin (V), m.p. 142—143°. p-Xyloquinone (modified prep.), new m.p. 124—125°, gives the quinol, m.p. 215—216°, the Me_2 ether, new m.p. 110—111°, of which with $\text{Zn}(\text{CN})_2\text{--HCl}\cdot\text{C}_6\text{H}_6$ gives 3:6-dimethoxy-2:5-dimethylbenzaldehyde, m.p. 59—60° (oxime, m.p. 118—119°); this did not yield a homogeneous Br-derivative; with $\text{CH}_2(\text{CO}_2\text{H})_2$ it gives 3:6-dimethoxy-2:5-dimethylbenzylidenemalonic acid, m.p. 195° (evolution of CO_2 ; after resolidification melts at about 215°), or on long heating 3-carboxy-6-methoxy-5:8-dimethylcoumarin, m.p. 229—230°, also obtained by fusion of the malonic acid. m-Xyloquinone (prep. from mesidine), m.p. 74—75°, gives similarly 3:6-dimethoxy-2:4-dimethylbenzaldehyde, m.p. 145°, which with $\text{CH}_2(\text{CO}_2\text{H})_2$ and piperidine in cold EtOH (3 days) gives 6-hydroxy-3-carboxy-5:7-dimethylcoumarin, m.p. 235—236° [is not smoothly debrominated; also obtained from (V) by FeCl_3], the Et ester, m.p. 165—166° [could not be obtained from the aldehyde by $\text{CH}_2(\text{CO}_2\text{Et})_2$], of which is hydrogenated to (V). $\text{CH}_2(\text{CO}_2\text{Et})_2$, (I), and $\text{Mg}(\text{OEt})_2$ in EtOH give a Mg compound, which with HCl affords (II), but with Me_2SO_4 in MeOH yields 3-bromo-5-hydroxy-2-methoxy-4:6-dimethylbenzylidenemalonic acid, m.p. 240—241° [unchanged by $\text{HCl}\cdot\text{COMe}_2$; gives (III) with $\text{HBr}\cdot\text{AcOH}$; with $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$ gives a substance, m.p. 187—188°, and with pure AcCl affords 3-bromo-5-hydroxy-2-acetoxy-4:6-dimethylbenzylidenemalonic acid, m.p. 231—232°, converted by $\text{Me}_2\text{SO}_4\text{--KOH}\cdot\text{MeOH}$ into the Me ether of (III).

R. S. C.

Heterocyclic compounds. I. Coumarins from 2-carbethoxycyclopentanone and 2-carbethoxy-4-methylcyclopentanone. S. Z. AHMAD and R. D. DESAI (Proc. Indian Acad. Sci., 1937, 5, A, 277—284).—2-Carbethoxycyclopentanone (I), H_2SO_4 , and PhOH yield cyclopenteno-1':2':4:3-coumarin, m.p. 129°. Similarly, the following are prepared: from p-cresol, 6-methyl-, m.p. 173—174°, from m-cresol, 7-methyl-, m.p. 247°, from resorcinol, 7-hydroxy- (II), m.p. 247° (acetate, m.p. 158—159°; benzoate, m.p. 166—167°), from 4-ethylresorcinol, 7-hydroxy-6-ethyl-, m.p. 266° (acetate, m.p. 168°), cyclopenteno-1':2':4:3-coumarin. Similarly, with (I) and POCl_3 , 4:6-diethylresorcinol yields 5-hydroxy-6:8-diethyl-, m.p. 195°, orcinol, 5-hydroxy-7-methyl-, m.p. 253—254° (acetate, m.p. 139—140°), phloroglucinol, 5:7-dihydroxy- (III), m.p. 273° (diacetate, m.p. 140°), and pyrogallol, 7:8-dihydroxy-, m.p. 270° (diacetate, m.p. 194°), cyclopenteno-1':2':4:3-coumarin. (I) and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$ with H_2SO_4 afford cyclopenteno-1':2':4:3- α -naphthapyrone, m.p. 218°. With 2-carbethoxy-4-methylcyclopentanone and H_2SO_4 , resorcinol yields 7-hydroxy- (IV), m.p. 173° (acetate, m.p. 143—144°), and 4-ethylresorcinol, 6-ethyl-7-hydroxy- (V), m.p. 198° (acetate, m.p. 116°), -4'-

methylcyclopenteno-1':2':4:3-coumarin, whilst α - $C_{10}H_7$ -OH affords 4'-*methylcyclopenteno-1':2':4:3-1:2- α -naphthapyrone*, m.p. 167°. Similarly, with $POCl_3$, *oreinol* affords 5-hydroxy-7-methyl- (VI), m.p. 215—216° (acetate, m.p. 107—108°), 4:6-diethylresorcinol, 5-hydroxy-6:8-diethyl-, m.p. 181—182°, *phloroglucinol*, 5:7-dihydroxy- (VII), m.p. 273° (diacetate, m.p. 133—134°), and *pyrogallol*, 7:8-dihydroxy-, m.p. 240° (diacetate, m.p. 118—119°), -4'-*methylcyclopenteno-1':2':4:3-coumarin*. The coumarins (II)–(VII) with $Hg(OAc)_2$ afford 6:8-bisacetoxymercuro-derivatives. J. D. R.

Review of methods used for distinguishing chromones from coumarins. G. R. KELKAR (Rasāyanam, 1936, 1, 68—74).—Chromones and coumarins can be distinguished by degradation to an *o*-OH-ketone or -acid or an *o*-methoxycinnamic acid, or, for 2-methylchromones, by formation of a styrene derivative, but negative results are in all cases inconclusive. R. S. C.

Syntheses in the 5-hydroxybenzopyrone group. I. 5-Hydroxy-2-methylchromone. D. B. LIMAYE and G. R. KELKAR (Rasāyanam, 1936, 1, 24—29).—5-Hydroxy-3-acetyl-2-methylchromone (I) (A., 1936, 855) when boiled with dil. Na_2CO_3 or NaOH yields 5-hydroxy-2-methylchromone, m.p. 92° [isolated from dil. AcOH, or from the Na salt, also obtained from (I) and NaOEt] (Ac, m.p. 108—110°, and Bz, m.p. 149°, derivatives), hydrolysed (dil. NaOH) to γ -resorecylic acid. 2-Acetylresorcinol Me ether and NaOAc-Ac₂O at 160—170° give 5-methoxy-3-acetyl-2-methylchromone, m.p. 149—151°, demethylated ($AlCl_3$) to (I), and hydrolysed to 2-hydroxy-6-methoxybenzoic acid (J.C.S., 1915, 107, 838). The above chromones do not condense with PhCHO, nor does 7-hydroxy-3-acetyl-2-methylchromone. 7-Hydroxy-2-methylchromone, however, gives a benzylidene derivative, m.p. 188—190°. E. W. W.

Influence of an acyl group in the 3-position on reactions of chromones. I. Action of aluminium chloride on 7-acetoxy-3-acetyl-2-methylchromone and a critical examination of the work of Wilson Baker. G. R. KELKAR and D. B. LIMAYE (Rasāyanam, 1936, 1, 60—64).—Contrary to statements of Baker *et al.* (A., 1934, 410; 1935, 80), 7-acetoxy-3-acetyl-2-methylchromone is deacetylated by $AlCl_3$ in $PhNO_2$ to give 7-hydroxy-3-acetyl-2-methylchromone and thence by alkali yields an acid, decarboxylated to 1:3:2-(OH)₂C₆H₃·COMe, whilst 7-hydroxy-8-acetyl-2-methylchromone and aq. NaOH give 2:4-diacetylresorcinol. 3-Acetyl- α -acetoxy-2-methylchromones are hydrolysed in the Fries reaction, whereas similar chromones without the Ac in position 3 rearrange normally. R. S. C.

Monohydroxyphenylxanthenes. J. B. NIEDERL and W. F. HART (J. Amer. Chem. Soc., 1937, 59, 719—720).—Xanthhydrol and the appropriate phenol in AcOH at 100° or with H_2SO_4 at 0° or $AlCl_3$ in hot C_6H_6 , followed, if necessary, by methylation, give 9-*p*-hydroxy-, m.p. 150° (Me ether, m.p. 112—113°; benzoate, m.p. 183—184°), -5'-chloro-2'-hydroxy-, m.p. 132°, and -2'-hydroxy-5'-acetyl-, m.p. 189°, -3'-methoxy-5'-tert.-phenylisobutyl-, m.p. 210°, and -2'-methoxy-5'-tert.- β -phenylamyl-xanthen, m.p. 202°, and

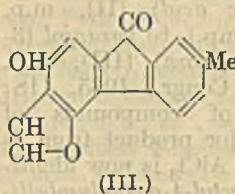
1-hydroxy- α -xanthyl-naphthalene, m.p. 195°. The products have PhOH coeff. <1. The compounds named have weak oestrogenic activity. R. S. C.

Synthesis of 1:2:3:4-dibenzoxanthone. E. GHIGI (Ber., 1937, 70, [B], 742—744; cf. A., 1936, 1511).—9-Hydroxyphenanthrene (I) and *o*-OH-C₆H₄-CO₂H (II) are transformed by P_2O_5 in $CHCl_3$ into 9-phenanthryl salicylate, m.p. 142°, converted when rapidly heated into 1:2:3:4-dibenzoxanthone, m.p. 209°, also obtained in small yield and mixed with much PhOH and phenanthrene when a mixture of (I), (II), and Ac_2O is heated to dryness. Treatment of (I) with NaOMe and then with *o*-C₆H₄Cl-CO₂K and Cu powder at 150—200° gives a mixture of products among which diphenic acid is identified. H. W.

Anisoxide. I. R. W. JACKSON and R. F. SHORT (J.C.S., 1937, 513—516).—From star aniseed oil, anisoxide (I), $C_{14}H_{18}O$, m.p. 41°, b.p. 140°/11 mm., a highly unsaturated cyclic ether, has been isolated (additive compound with maleic anhydride, decomp. 280°). Catalytic reduction (H_2 -PtO₂) of (I) gives perhydroanisoxide (II), b.p. 120—122°/10 mm., and reduction with Na-EtOH yields dihydroanisoxide (III), b.p. 120—122°/10 mm. Oxidation of (I) with air or O_3 affords MeCHO and with $KMnO_4$ gives an acid, $C_{12}H_{14}O_3$, m.p. 181—182° (anilide, m.p. 155—156°), further oxidised to an acid, $C_{11}H_{10}O_3$, m.p. 215—216°, and subsequently to an acid, $C_{11}H_{10}O_4$, m.p. 179.5—180.5° (Me ester, m.p. 79—80°), containing 1 OH. The oxide ring in (II) is broken by HBr to give a dibromide, $C_{14}H_{26}Br_2$, converted into the unsaturated hydrocarbon, $C_{14}H_{24}$, b.p. 110—112°/10 mm., which is oxidised (O_3) to a mixture from which a ketone, b.p. 102—105°/10 mm. (semicarbazone, m.p. 161—162°), is separated. (III) is oxidised ($KMnO_4$) to a ketone, $C_{14}H_{18}O_2$ (semicarbazone, m.p. 191—192.5°). A paraffin hydrocarbon, $C_{19}H_{40}$, m.p. 45—46°, has also been separated from the oil. F. R. S.

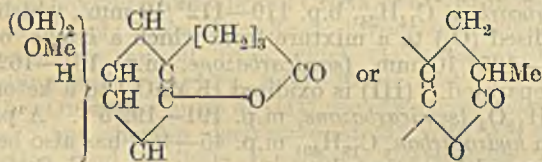
Syntheses in the naphthalene group. II. Heterocyclic analogues of the 4-hydroxy-1-aryl-2-naphthoic acids. W. BORSCHKE and H. LEDITSCHKE (Annalen, 1937, 529, 108—114).—Furyl *p*-tolyl ketone, b.p. 180—183°/23 mm., m.p. 41—42°, condenses with Et₂ succinate (I) to a dark brown resin which is cyclised by Ac_2O and NaOAc and then de-acetylated and hydrolysed to 4-hydroxy-1-furyl-6-methyl-2-naphthoic acid, m.p. 196—198° (Me ester, m.p. 206°), and 3-hydroxy-6-*p*-tolylcoumarone-5-carboxylic acid (II), m.p. 234° [Ac derivative, m.p. 238°; Me ester, m.p. 172°, and its Ac derivative, m.p. 120°; 3-hydroxy-4-benzeneazo-6-*p*-tolylcoumarone-5-carboxylic acid, m.p. 199° (decomp.)]. When heated in quinoline containing Cu bronze (II) passes into 3-hydroxy-6-*p*-tolylcoumarone, b.p. 170—172°/0.1 mm., m.p. 110°.

With conc. H_2SO_4 at room temp. (II) gives 9-keto-7-hydroxy-2-methyl-5:6:2':3'-furanofluorene (III), m.p. 278°. Furyl *p*-anisyl ketone, m.p. 63°, is transformed by (I) and NaOEt into *b*-Et γ -2-furyl- γ -*p*-anisylitaconate, m.p. 146°, cyclised to 3-hydroxy-6-*p*-anisylcoumarone-5-carboxylic acid, m.p. 256°



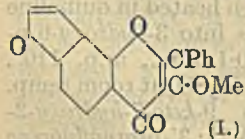
(*PhN*₂-derivative, decomp. 219°). (I) and *furyl* 3 : 4 : *dimethoxyphenyl ketone*, m.p. 114°, yield a brown resin whence 3-hydroxy-6-3' : 4'-dimethoxyphenylcoumarone-5-carboxylic acid, m.p. 272°. (I) and 2-benzoylthiophen give as non-cryst. H ester, transformed into non-cryst. 4-hydroxy-1'-2'-thienyl-2-naphthoic acid (*PhN*₂-derivative, decomp. 237°). H. W.

Luganin. I. K. W. MERZ and K. G. KREBS (Arch. Pharm., 1937, 275, 217—236).—Luganin (I) (isolated in 1.7% yield from the pulp of *Strychnos nux vomica*), C₁₆H₂₂O₅·OMe, m.p. 222—223° (decomp.; rapid heating), [α]_D²⁰ −82.11° in H₂O [*Ac*, m.p. 142°, *Bz*, m.p. 157—158°, and (p-*NO*₂·C₆H₄·CO)₂ derivatives, m.p. 207—208°], has normal mol. wt. in H₂O, but not in other solvents. It contains a lactone group, neutralising 1 NaOH when heated, and its acyl derivatives consume 1 extra mol. of hot NaOH. It is hydrolysed by emulsin or acid to glucose (identified as osazone and penta-acetate) and *luganetin* (II), C₁₁H₁₆O₅, amorphous, [α]_D¹⁵ −23.71° in EtOH, but heating during hydrolysis causes decomp. As usually obtained (II) is very hygroscopic, but repeated evaporation of its Et₂O solution gives a less sol., non-hygroscopic dimeride (?). It gives a (CPh₃)₂, m.p. 155—156°, CPh₃, m.p. 115—117°, and (p-*NO*₂·C₆H₄·CO)₂ derivative, m.p. about 110°; with Se it gives traces of a cryst. substance, with KOH-H₂O₂ gives HCO₂H, AcOH, and possibly AcCO₂H; it is destroyed by other oxidising agents, absorbs 1 H₂ catalytically, and reacts slowly with aq. Br, possibly by substitution. When heated, (II) absorbs 2 mols. of NaOH and its acyl derivative absorbs an excess of



2 mols. Probably (II) is the lactone (above formulae) of a phenolic acid, (I) being the lactone of an alcoholic acid with the phenolic OH glucosidically bound. R. S. C.

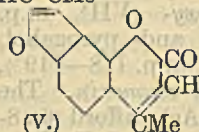
Syntheses in the furocoumarin group. II. The *karanjin* way of synthesising furocoumarins as illustrated on 5 : 4 : 7' : 8'-furocoumarin. D. B. LIMAYE. III. Formation of the linear 3 : 4'-dimethyl-4 : 5 : 6' : 7'-furocoumarin. D. B. LIMAYE and D. D. GANGAL (Rasāyanam, 1936, 1, 1—14, 15—23).—II. Oil from the seeds of the leguminous plant *karanja* (*Pongamia glabra*) contains *karanjin*, identified as 3'-methoxy-2'-phenyl-5 : 4 : 7' : 8'-furochromone (I), which is degraded through *karanjic acid* (3-hydroxybenzofuran-4-carboxylic acid) (II), m.p. 220° (decomp.), to *karanjol* (3-hydroxybenzofuran) (III), m.p.



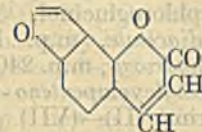
55—56° (cf. Proc. Indian Sci. Congr., 1935, 118; 1926, 151). The synthesis of compounds of type (I) is attempted. The major product from 4-methylumbelliferone acetate and AlCl₃ is now identified (cf. A., 1932, 521) as 8-acetyl-4-methylumbelliferone (IV), since it gives 2-acetylresorcinol (cf. A.,

1934, 298); the product from (IV) and NaOEt-CH₂Br·CO₂Et is thus 8-acetyl-7-carboxymethoxy-4-methylcoumarin, and that from the last and Ac₂O-NaOAc is not the *lin.*-furocoumarin (A., 1932, 521), but 3 : 4'-dimethyl-5 : 4 : 7' : 8'-furocoumarin (V).

HC CMe



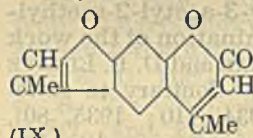
(V.)



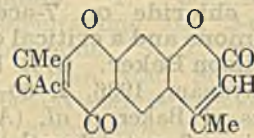
(VII.)

2 : 6-Dimethoxybenzaldehyde (A., 1935, 83) and AlCl₃-C₆H₆ at room temp. give 2-hydroxy-6-methoxybenzaldehyde (VI), m.p. 75° (semicarbazone, m.p. 250°), further demethylated to 2 : 6-dihydroxybenzaldehyde, m.p. 154—155°. With NaOEt-CH₂Br·CO₂Et, (VI) forms 2-aldehydo-3-methoxyphenoxycetic acid, m.p. 138°, converted (Ac₂O-NaOAc at 150°) into 3-methoxybenzofuran, b.p. 220—222°, also obtained by methylation of (III). With aq. NaHCO₃ at 120°, (III) gives (II); with NaOH-CHCl₃, (III) yields 3-hydroxybenzofuran-4-aldehyde, m.p. 60° (semicarbazone, m.p. 253°). This with NaOAc-Ac₂O at 170° yields 5 : 4 : 7' : 8'-furocoumarin (VII), m.p. 139—140°, of the same constitution as has been assigned (A., 1934, 780) to angelicin.

III. 4-Methylumbelliferone acetate and AlCl₃ at 160° yield [with 8-acetyl-4-methylumbelliferone (above)] 6-acetyl-4-methylumbelliferone (VIII), m.p. 210° (semicarbazone, m.p. >300°; *Me* ether, m.p. 209—210°; *Bz*, m.p. 160°, and *Ac*, m.p. 172°, derivatives), which with NaOEt-CH₂Br·CO₂Et (better yield from the *Na* derivative) gives 6-acetyl-7-carboxymethoxy-4-methylcoumarin, m.p. 183°. This is hydrolysed by NaOH-EtOH to the 7-carboxymethoxy-compound, m.p. 268—270° (decomp.), which is condensed by Ac₂O at 150—155° to the (linear) 3 : 4'-dimethyl-4 : 5 : 6' : 7'-furocoumarin (IX), m.p. 222°. With Ac₂O-NaOAc at 150—160° (VIII) gives 5-acetyl-6 : 4'-dimethyl-2 : 3 : 7' : 6'-(1 : 4-pyrone)-



(IX.)



(X.)

coumarin (X), m.p. 245°, hydrolysed to a substance, C₁₄H₁₂O₅, m.p. 262°, and an acid, m.p. 223—225°.

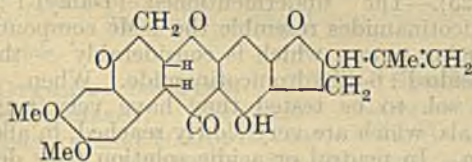
E. W. W.

Syntheses in the furocoumarin group. IV. General considerations on the synthesis of the third type of furocoumarin from resorcinol. D. B. LIMAYE (Rasāyanam, 1936, 1, 43—44; cf. preceding abstract).—General principles of this synthesis are discussed. R. S. C.

Identification of tephrosin and deguelin from different sources. J. J. BOAM, R. S. CAHN, and A. STUART (J.C.S.I., 1937, 56, 91—96t).—*allo*-Tephrosin (I) (Merz *et al.*, A., 1935, 221) is impure tephrosin (II); *isoallotephrosin* (III) is pure (II). *iso*Deguelin (IV) is identical with deguelin (V). *iso*Dehydrodeguelin is identical with dehydrodeguelin except in colour; the two forms are not interconvertible, but either may be given by most

methods of formation; the yellow colour of the isoform resists removal by C, crystallisation, etc., as does that of dehydrorotenone, which is obtained in the ordinary yellow form from rotenolone-II by Ac_2O - NaOAc , one of the few reactions which always gives the colourless dehydro-compound in the deguelin series. Crystallo-optical data, which are detailed for these substances and for the substance, m.p. 189° (now named *sumatrol*), obtained from Sumatratype *Derris* roots (Cahn *et al.*, B., 1935, 381), are essential for identification as m.p. are unreliable and variable in the rotenone series. Dihydrodeoxyisodeguelin and dihydroisoallotephrosin are correctly named *dihydrodeoxydeguelin* and *dihydrotephrosin*, respectively; dihydroallotephrosin was an impure form of the latter. Other derivatives of (IV) are identical with those of (V), and those of (I) and (III) with those of (II). In the normal methods of prep. either (II) or (V) or mixtures of both may be obtained from one sample of *Derris* or *Lonchocarpus nicou* in different experiments. Purification of (II) by crystallisation is often ineffective and is best achieved by hot NaOH - EtOH or NH_3 - EtOH . R. S. C.

Sumatrol. I. A. ROBERTSON and G. L. RUSBY (J.C.S., 1937, 497—503).—*Sumatrol* (I), $C_{21}H_{16}O_5(OMe)_2$, m.p. 194° , $[\alpha]_D -184^\circ$ in C_6H_6 , isolated from the resin of a species of *Derris* (cf. Cahn and Boam, B., 1935, 381), forms an *oxime*, m.p. $245-247^\circ$, cannot be dehydrated, and contains a phenolic OH *ortho* to CO. (I) is converted (I; Zn-AcOH) into *dehydrosumatrol* (II), m.p. $190-192^\circ$, $[\alpha]_D -55^\circ$ in $CHCl_3$ (*Ac* derivative, m.p. $256-259^\circ$). Hydrogenation (H_2 -Pt) gives *tetra*-, m.p. $222-223^\circ$, $[\alpha]_D +122^\circ$ in $CHCl_3$, and *di-hydrosumatrol*, m.p. $184-185^\circ$, $[\alpha]_D -32^\circ$ in $CHCl_3$. The H_2 -compound is converted into *dehydrodihydrosumatrol*, m.p. 235° , $[\alpha]_D -63^\circ$ in $CHCl_3$, and the H_4 -compound into *dehydrotetrahydrosumatrol*, m.p. 218° (*Ac*₂ derivative, m.p. 197°). (II) with KOH-EtOH adds 2 H_2O to give *sumatrollic acid*, m.p. 150° . By analogy with the rotenone series, the following formula is suggested for (I).



F. R. S.

l-Asarinin, a new constituent of varieties of *Asarum*. I. Constitution of l-asarinin. T. KAKU, N. KUTANI, and J. TAKAHASHI (Keijo J. Med. 1936, 7, 644–656).—*Asarum sieboldi*, Miquel, and its variety *seoulensis*, Nakai, contain l-asarinin, $C_{20}H_{20}O_6$ (I), m.p. 122–123°, $[\alpha]_D^{20}$ –118.6° (all rotations in $CHCl_3$), which is not attacked by aq. KOH at the b.p., but with KOH–NaOH at 250° slowly yields protocatechuic acid. $KMnO_4$ – Ac_2O gives piperonal and piperonylic acid, and HNO_3 (*d* 1.48)– $AcOH$ forms dinitro-l-asarinin, m.p. 220–221°, $[\alpha]_D^{18}$ +30.6°, and 4-nitro-1:2-methylenedioxybenzene (II), new m.p. 148°; more energetic oxidation gives (II), 6-nitropiperonal, and $H_2C_2O_4$. $EtOH$ – HCl partly isomerises (I) into l-sesamin, m.p. 122–124°, $[\alpha]_D^{17}$

-68.1°. Sesamin (A., 1929, 298) is renamed d-*sesamin*, and dl-*sesamin*, m.p. 129–130°, $[\alpha]_D^{20}$ 0°, is prepared. Dinitro-d-, m.p. 240–241°, $[\alpha]_D^{19} +35.1^\circ$, and l-*sesamin*, m.p. 240–241°, $[\alpha]_D^{19} -34.5^\circ$, are obtained, with (II). Dinitro-dl-*sesamin*, m.p. 223°, has $[\alpha]_D^{20}$ 0°. d-*Sesamin* with EtOH-HCl at 100° is partly isomerised into d-*asarinin*, m.p. 122–123°, $[\alpha]_D^{19} +119.1^\circ$ [$(NO_2)_2$ -derivative, m.p. 220–221°, $[\alpha]_D^{17} -29.5^\circ$]; dl-*asarinin*, m.p. 135–136°, and dinitro-dl-*asarinin*, m.p. 223°, have $[\alpha]_D^{20}$ 0°. l-*Asarinin* is saturated, and does not contain a ketone group. The alternative structures $\text{CHR} \begin{array}{c} \diagup \text{O} \cdot \text{CH} \cdot \text{CHR} \\ \diagdown \text{CH} \cdot \text{CH} \cdot \text{O} \end{array} \text{CH}_2$ and $\text{O} \begin{array}{c} \diagdown \text{CH} \cdot \text{CH} \cdot \text{CHR} \\ \diagup \text{CHR} \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{O}$ ($\text{R} = \text{C}_6\text{H}_3 \cdot \text{O}_2\text{CH}_2$) are proposed.

E. W. W.

Action of alkali disulphides on tetrabromotetramethylmethane. H. J. BACKER and N. EVENHUIS (Rec. trav. chim., 1937, **56**, 129—136).—Interaction of $C(CH_2Br)_4$ with K_2S_2 or Na_2S_2 in boiling EtOH affords 2 : 6 : 7-trithia-4-spirooctane 2-sulphide (I), $\begin{matrix} S-CH_2 \\ | \\ S-CH_2 \end{matrix} > C < \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > S:S$, m.p. 78.5°, which yields cryst. compounds + $HgCl_2$ and + $HgBr_2$ and when refluxed with Cu-PhMe gives 2 : 6 : 7-trithia-4-spirooctane, m.p. 55.5—56.5° ($HgCl_2$ and $HgBr_2$ additive compounds). (I) is oxidised by BzO_3H in $CHCl_3$ to 2 : 6 : 7-trithia-4-spirooctane 2 : 2 : 6 : 6-tetroxide, m.p. 257° (decomp.), and H_2SO_4 , and by H_2O_2 -AcOH to 1-thia-3 : 3-disulphodimethylcyclobutane 1 : 1-dioxide + $2H_2O$, $SO_2 < \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > C(CH_2 \cdot SO_3H)_2 \cdot 2H_2O$ (Ba salt + $3H_2O$; Tl salt). The corresponding 3 : 3-dimethyldisulphonyl dichloride, m.p. 144—146°, yields a diamide, m.p. 200—202°. Similarly $CMe_3(CH_2Br)_2$ when refluxed (3 hr.) with K_2S_2 -EtOH gives 4 : 4-dimethyl-1 : 2-dithiacyclopentane, $CMe_2 < \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > S$, b.p. 128—129°/27 mm., which polymerises to a white solid when heated and is oxidised by $AcOH-H_2O_2$ to $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -disulphonic acid (Tl salt + H_2O), isolated as the Ba salt (+ H_2O). H. G. M.

Catalytic transformation of heterocyclic compounds. VI. Comparison of action of catalysts in the simultaneous dehydration of furan and ammonia. J. K. JURIEV and P. M. RAKITIN (J. Gen. Chem. Russ., 1937, 7, 485—491).—The activity of a no. of catalysts of the reaction of production of pyrrole (I) from furan and NH_3 at 350—600° falls in the order $\text{Al}_2\text{O}_3 > \text{ThO}_2 > \text{MgSO}_4 > \text{C} > \text{Fe}_2\text{O}_3$; max. yields (40%) of (I) are obtained with Al_2O_3 at 550°. The mechanism of the reaction is discussed.

R. T.

2-Methyl-4-*n*-amylpyrrole. F. WREDE (Arch. exp. Path. Pharm., 1937, 184, 327—330).—Et *n*-octoylacetate (prep. from heptaldehyde) when treated with NaNO_2 , reduced with Zn, and condensed with $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ gave *Et*, 2-methyl-4-*n*-amylpyrroledicarboxylate, m.p. 85° , which when distilled over soda-lime yielded 2-methyl-4-*n*-amylpyrrole (I), b.p. $130^\circ/10$ mm., reduced ($\text{Pd}-\text{C}-\text{H}_2$ in AcOH) to 2-methyl-4'-*n*-amylpyrrolidine [platinichloride, $(\text{C}_{10}\text{H}_{21}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, m.p. 140° ; aurichloride, an oil]. The pyrrole $\text{C}_{10}\text{H}_{17}\text{N}$

derived by oxidative breakdown of prodigiosin is not (I).
P. W. C.

3-Aminopiperidine. H. NIENBURG (Ber., 1937, 70, [B], 635—638).—3-Aminopyridine hydrochloride is quantitatively reduced (PtO₂ in MeOH) to 3-aminopiperidine dihydrochloride (I), m.p. 225° after softening at 180° (corresponding *dipicrate*, decomp. 258°, and *platinichloride*, C₅H₁₂N₂·H₂PtCl₆), which is stable towards KMnO₄ at room temp. (I) and NaOEt in MeOH-EtOH yield 3-aminopiperidine, b.p. 68°/17 mm., 168—170°/760 mm., m.p. 55—57° [Bz₂, m.p. 197°, and *dicarbamyl*, m.p. 213° (decomp.)], derivatives].
H. W.

Association of α -piperidone. G. I. JENKINS and T. W. J. TAYLOR (J.C.S., 1937, 495—497).—Measurements of apparent mol. wt. of α -piperidone in H₂O show little sign of association, but in C₆H₆ the val. is 1.75 times the formula wt. at low dilution and approximates to 2 as concn. increases. This indicates that the association takes place by H-bond formation to give a dimeric form. This is discussed with reference to the linkings in a polypeptide chain.
F. R. S.

Conductivities and potentials of higher alkylpyridinium chlorides.—See A., I, 309.

"Acid fissions," particularly of certain pyridinium salts. F. KRÖHNKE and W. HEFFE (Ber., 1937, 70, [B], 862—878).—Study of the rate of fission of many phenacylpyridinium salts by NaOH at 20° shows that negative substituents in the *m*- or *p*-position in the C₆H₅ nucleus accelerate whereas positive substituents retard hydrolysis. Hydrolysis of salts which do not yield *o*-substituted aromatic acids depends on the dissociation const. of the latter. *o*-Substituents cause great retardation due to steric influences, the effect being particularly noticeable in the C₁₀H₈ series. Di-*o*-substituted compounds do not undergo hydrolysis. Fission is hampered by positive, facilitated by negative, substituents in the C₅H₅N nucleus. Hydrolysis occurs much more rapidly in H₂O than in EtOH. Salts substituted in the CH₂ by acyl residues are hydrolysed with difficulty by alkali, with ease by acids whereby acalkylcycloammonium salts are produced. Salts substituted in the CH₂ by alkyl are much more readily hydrolysed than the unsubstituted salts; in this respect the phenacylpyridinium salts resemble 1:3-diketones, CH₂Ac·CO₂Et, and many other compounds all of which contain the group :CX·C'O (X=S, N, or O). Phenacylpyridinium bromide is converted by dioxan (containing peroxides) into methylenedipyridinium bromide (H₂O₂ in neutral solution containing a suitable acceptor can oxidise Br' to Br). The following *-phenacylpyridinium bromides* are described; *p*-methyl-, m.p. 205° (decomp.) [ω -Br-derivative, m.p. 180° (decomp.)]; 3-nitro-4-methyl-, m.p. 217—218° (decomp.); 3-bromo-4-methyl-, m.p. 215—217° (decomp.); 3:4-dimethyl-, m.p. 232—233° (decomp.); 2:4-di-methyl-, m.p. 210° (decomp.); 2:4:6-trimethyl-, m.p. 273° (decomp.) [*perchlorate*, m.p. 273° (decomp.); *nitrate*]; 2:3:5:6-tetramethyl-, decomp. >280° (corresponding *enol-betaine*, m.p. 190—191°); *p*-methoxy-, m.p. 203—204° (decomp.) (corresponding *perchlorate*, m.p. 199°, and *enol-betaine*, m.p. 96°);

3-bromo-4-methoxy-, m.p. 224—225° [corresponding *perchlorate*, m.p. 187—189°, and *enol-betaine*, m.p. 97° (incipient decomp. 93°)]; *p*-phenoxy-, m.p. 168—170°, and the corresponding *enol-betaine*, m.p. 105—108°; *p*-nitro-, m.p. 245—247° (decomp.); *m*-chloro-, decomp. about 250° (corresponding *perchlorate*, m.p. 198—199°); *o*-chloro-, m.p. 211° (decomp.) (corresponding *perchlorate*, m.p. 176—177°); *o*-bromo-, m.p. 213° (decomp.); 2:5-dichloro-, m.p. 271° (decomp.) (corresponding *perchlorate*, m.p. 237—238°); 2:6-dichloro-, m.p. 280—281° (decomp.) (corresponding *perchlorate*, decomp. >280°). 3-Bromopyridine and CH₂BzBr afford 3-bromo-1-phenacylpyridinium bromide, m.p. 209—211° (decomp.), which gives an *enol-betaine*, m.p. 118—119° (decomp.). 3-Bromo-1-*p*-bromophenacylpyridinium bromide, decomp. 245.5°, gives an *enol-betaine*, m.p. 134—135° (decomp.). Phenacyl-3:5-dibromopyridinium bromide, m.p. 220—221° (decomp.) (also *hydrate*) and the *enol-betaine*, decomp. 115°, are described. 2-Chloropyridine and CH₂BzBr yield phenacyl-2-chloropyridinium bromide (+H₂O), m.p. 179°, transformed by NaOH into 1-phenacyl-2-pyridone, m.p. 154.5° (*perchlorate*, m.p. 131° after softening at 125°). Phenacylpyridinium sulphate, m.p. 236°, and *H* sulphate, m.p. 203—204°, are described. *p*-isoPropylphenacylpyridinium perchlorate has m.p. 182.5°.
H. W.

Manufacture of bases derived from 2-aminopyridine.—See B., 1937, 421.

Constitution of products of sulphonation of 3-amino- and 3-hydroxy-pyridine. E. PEŁAZEK (Rocz. Chem., 1937, 17, 97—100).—5-Nitro-2-thiopyridine in aq. NH₃ and KMnO₄ at 100° yield chiefly the *K* salt of 5-nitropyridine-2-sulphonic acid (I), m.p. 302—304°, together with 5-nitro-2-aminopyridine (II), m.p. 186—188°, also obtained from (I) and SnCl₂. The product of sulphonation of 3-aminopyridine (A., 1934, 1009) must be 3-aminopyridine-2-sulphonic acid, since it is not (I).
R. T.

1-Alkyl-1:6-dihydronicotinamides. P. KARRER and F. J. STARE (Helv. Chim. Acta, 1937, 20, 418—423).—The undermentioned 1-alkyl-1:6-dihydronicotinamides resemble the 1-Me compound (I) in reducing power, which is considerably > that of 1-glucosido-1:6-dihydronicotinamide. When sufficiently sol. to be tested they have very negative potentials, which are very slowly reached, in alkaline solution. In neutral or acidic solution they decompose immediately giving non-cryst., very hygroscopic substances apparently formed by addition of acid which in the adduct is devoid of ionogenic properties. This property is explained by the presence of a conjugated system of double linkings which also permits the union with maleic anhydride to uninviting adducts. The absorption spectrum has a characteristic max. at 365 m μ . Nicotinamide is transformed by boiling EtI into the corresponding *ethiodide*, m.p. 198°, reduced by Na₂S₂O₄ and Na₂CO₃ to non-cryst. 1-ethyl-1:6-dihydronicotinamide and a substance, m.p. 220—230° (decomp.). The following are prepared analogously: *nicotinamide propiodide*, m.p. 182°, and 1-propyl-1:6-dihydronicotinamide, m.p. 96° after softening; *nicotinamide butiodide*, m.p. 152—153°, and 1-butyl-1:6-dihydronicotinamide which crystallises

when strongly cooled; *nicotinamide benzylchloride*, m.p. 236° (decomp.), and 1-benzyl-1:6-dihydronicotinamide, m.p. 123° after softening at about 115°; *nicotinamide cetochochloride*, m.p. 235° (decomp.), and 1-cetyl-1:6-dihydronicotinamide, m.p. 54°.

[With J. F. BARTLETT.] (I) is hydrogenated (PtO₂ in H₂O) to 1-methylhexahydronicotinamide, m.p. 95°.

H. W.

Oxidation product of adrenaline. D. RICHTER and H. BLASCHKO (J.C.S., 1937, 601—602).—The red product formed by oxidising *l*-adrenaline with KIO₃ has been isolated; it is probably 2-iodo-3-hydroxy-1-methyl-2:3-dihydroindole-5:6-quinone.

F. R. S.

Organic catalysts. XV. Synthetic carboxylases. V. W. LANGENBECK and O. GÖDDE (Ber., 1937, 70, [B], 669—671; cf. A., 1934, 1229; 1936, 1471).—The data 0.64, 1.48, 0.79, 0.20, 1.18, 1.59, 1.32, and 1.00 are recorded for the activity vals. of 5-aminonaphthoxindole, its 6-, 7-, and 8-OH- and 5-, 6-, 7-, and 8-Me derivatives, respectively. 1:4-C₁₀H₆Me·NH₂ and (OH)₂C(CO₂Et)₂ in AcOH at room temp. yield *Et* 5-methyl-1-naphthadioxindolecarboxylate, m.p. 220° (decomp.), converted by successive hydrolysis, treatment with air, and acidification into 5-methyl-1-naphthhisatin, decomp. (indef.) >230°, the *oxime*, m.p. 240°, of which is reduced by SnCl₂ and conc. HCl in AcOH at 100° to 3-amino-5-methyl-1-naphthoxindole hydrochloride. 1:5-C₁₀H₆Me·NH₂ yields analogously *Et* 6-methyl-1-naphthadioxindolecarboxylate, m.p. 215° (decomp.), which gives successively 6-methyl-1-naphthadioxindole, 6-methyl-1-naphthhisatin, m.p. 257° (decomp.), its *oxime*, m.p. 277°, and 3-amino-6-methyl-1-naphthoxindole hydrochloride, which is stable in air. 2:5-C₁₀H₆Me·NH₂ affords successively *Et* 7-methyl-1-naphthadioxindolecarboxylate, m.p. 196° (decomp.), 7-methyl-1-naphthhisatin, m.p. about 265° after darkening, 7-methyl-1-naphthhisatinoxime, m.p. 274°, and 3-amino-7-methyl-1-naphthoxindole hydrochloride, decomp. >185°. Similarly, 2:8-C₁₀H₆Me·NH₂ yields *Et* 8-methyl-1-naphthadioxindolecarboxylate, 8-methyl-1-naphthhisatin, m.p. 254° (decomp.), 8-methyl-1-naphthhisatinoxime, m.p. 250°, and 3-amino-8-methyl-1-naphthoxindole hydrochloride.

H. W.

Organic catalysts. XVI. Synthetic dehydrogenases. III. W. LANGENBECK, L. WESCHKY, and O. GÖDDE (Ber., 1937, 70, [B], 672—674; cf. A., 1927, 546).—The dehydrogenase activity towards *dl*-alanine of isatin-4- and -6-carboxylic acid is 20 times that of isatin (*loc. cit.*). Activity of the catalysts is enhanced 100-fold when dil. C₅H₅N containing some AcOH is substituted for dil. AcOH as solvent. The acids are nearly thrice as active as the yellow enzyme.

H. W.

Derivatives of 3-nitro-4-hydroxyquinoline. M. COLONNA (Gazzetta, 1937, 67, 46—53).—3-Nitro-4-hydroxyquinoline yields (Me₂SO₄ etc.) 3-nitro-4-methoxy-, m.p. 220°, -4-ethoxy-, m.p. 202°, -4-propoxy-, m.p. 156°, and -4-butoxy-quinoline, m.p. 140°, reduced (Sn-HCl) to 3-amino-4-methoxy- [hydrochloride, m.p. 155° (decomp.)]; *Ac* derivative, m.p. 216°, -4-ethoxy- [hydrochloride, m.p. 165° (resolidifying 168°, remelting 218°); *Ac* derivative, m.p. 160°], -4-propoxy- [hydro-

chloride, decomp. 215°; *Ac* derivative, m.p. 177—178°], and -4-butoxy-quinoline [hydrochloride, decomp. 283°; *Ac* derivative, m.p. 135—136°].

o-NH₂·C₆H₄·CO₂Me in HCl with NO₂·CH₂·CH·N·OH yields *Me o*-β-nitroethylideneaminobenzoate (I), m.p. 153°, which when boiled with Ac₂O-NaOAc forms a substance [additive product of (I) and Ac₂O?], m.p. 113—114°, hydrolysed (HCl) to (I), but does not condense to the quinoline.

E. W. W.

Salts of bivalent silver. Quinolate of Ag^{II}. (MLLE.) A. BURADA (Ann. Sci. Univ. Jassy, 1935, 20, 71—74).—C₅H₃N(CO₂)₂Ag, C₅H₃N(CO₂H)₂·2H₂O (I), which contains Ag^{II}, has been prepared by the oxidation of Ag(C₉H₇N)₂NO₃ by (NH₄)₂S₂O₈ or from AgNO₃ + quinolinic acid + K₂S₂O₈. It forms sparing sol. red crystals, gives a blue colour with NPh₂ in H₂SO₄, oxidises alkali halides to halogens, AgCl being formed, and is decolorised by NH₃ and H₂O₂.

R. S. B.

Acridine. XVI. Preparation of 2- and 4-substituted acridones from 3'-substituted diphenylamine-2-carboxylic acids. K. LEHMSTEDT and K. SCHRADER (Ber., 1937, 70, [B], 838—849).—3'-Methoxydiphenylamine-2-carboxylic acid is transformed by POCl₃ at 100° into a mixture of 5-chloro-2-methoxy- (I), m.p. 170°, and 5-chloro-4-methoxy- (II), m.p. 124—125°, *acridine*. (I) is converted by long heating with 20% H₂SO₄ at 100° into 2-methoxyacridone, m.p. 273°, whilst (II) with *N*-HCl readily affords 4-methoxyacridone, m.p. 346°. Ring-closure of the acid can also be effected by conc. H₂SO₄ at 100° but is accompanied by sulphonation, the effect of which is removed by after-treatment with boiling 50% H₂SO₄. 3'-Methyldiphenylamine-2-carboxylic acid gives a mixture of chloromethylacridines from which 2-methylacridone, m.p. 312°, is isolated by short treatment with *N*-HCl at 100°, whilst further heating of the filtrate leads to 4-methylacridone, m.p. 336°. 3'-Chlorodiphenylamine-2-carboxylic acid yields 2:5-dichloroacridine, m.p. 169—170°, and 4:5-dichloroacridine, m.p. 116—117°, converted by NPhMe₂ and POCl₃ at 100° into 4-chloro-5-*p*-dimethylaminophenylacridine, m.p. 252—253°, and by *N*-HCl into 4-chloroacridone, m.p. >360°. 3'-Nitrodiphenylamine-2-carboxylic acid affords 5-chloro-2-nitroacridine, m.p. 214°, and 5-chloro-4-nitroacridine, m.p. 140—141°, whence 4-nitro-5-*p*-dimethylaminophenylacridine, m.p. 280—281°, and 4-nitroacridone. 4-Aminoacridone blackens at about 275°.

H. W.

Manufacture of 4:5-dihydroglyoxalines.—See B., 1937, 422.

Higher-melting crystals from solutions of picrolonic acid. L. KOFLER and F. A. MÜLLER (Mikrochem., Molisch Festschr., 1936, 271—273).—Solutions of technical picrolonic acid deposit small amounts of unknown crystals of two characteristic habits, (a) m.p. 200—250°, (b) decomp. 150—180°.

J. S. A.

New synthetic method in the pyrazole group. I. R. FUSCO and R. JUSTONI (Gazzetta, 1937, 67, 3—10).—Halogenohydrazones, CRX·N·NHR, and *Na* derivatives of cyanoketones, β-diketones, or β-ketonic esters, form pyrazoles. Thus α-chlorobenzaldehyde-phenylhydrazone (I) with the *Na* derivative of

CN·CH₂Ac gives 4-cyano-1:3-diphenyl-5-methylpyrazole, m.p. 134°, hydrolysed to the 4-carboxylamide, m.p. 232°, and thence to the acid; with CN·CH₂·COBu⁷ 4-cyano-1:3-diphenyl-5-tert-butylpyrazole, m.p. 163—164°, hydrolysed, with difficulty, to the 4-carboxylamide, m.p. 211° [also obtained from (I) and the Na derivative of COBu⁷·CH₂·CO·NH₂], which could not be further hydrolysed; and, with CN·CH₂Bz, 4-cyano-1:3:5-triphenylpyrazole, hydrolysed to the 4-carboxylamide, m.p. 197° (similarly obtained from CH₂Bz·CO·NH₂), and to the acid. E. W. W.

Sodium phenylethylbarbiturate solution for injection. L. NIELSEN (Dansk Tidsskr. Farm., 1937, 11, 65—77).—The decomp. 5-phenyl-5-ethylbarbituric acid + H₂O → CHPhEt·CO·NH·CO·NH₂ (I) + CO₂, (I) + H₂O → CHPhEt·CO₂H + CO(NH₂)₂ (II), (II) + H₂O → CO₂ + 2NH₃, NH₃·CO₂Et (III) + H₂O → CO₂ + NH₃ + EtOH (IV), (III) + H₂O ⇌ (IV) + (II) + CO₂, have been studied in solution at room temp. and 80°. Apparatus for the determination of small quantities of CO₂ is described. M. H. M. A.

Substituted barbituric acids.—See B., 1937, 499.

Multivalent amino-acids and peptides. VIII. Synthesis of bisanhydro-l-cystinyl-l-cystine and other diketopiperazines of cystine. (Miss) J. P. GREENSTEIN (J. Biol. Chem., 1937, 118, 321—329).—An attempt to prepare a polymeride of anhydro-cysteinylcystine in which dimethyldiketopiperazine rings would form a repeating pattern yielded only a dimeride. The acid chloride (I) from dicarbobenzyloxy-cystine combines in CHCl₃ with cysteine Et ester hydrochloride to form Et₂ di(carbobenzyloxy)-l-cystyl-di-l-cystinate, m.p. 72—76°, which with PH₄I yields cysteinylcystine Et ester hydriodide, converted by NH₃-EtOH into anhydro-l-cystinyl-l-cystine, SH·CH₂·CH<NH·CO>CH·CH₂·SH, m.p. 208° (decomp.), [α]_D²⁵ −62.5° in H₂O (converted by cold conc. HCl into cysteinylcystine hydrochloride, m.p. 158°, [α]_D²⁵ +44.8°, oxidised to cystinylcystine). This is oxidised by H₂O₂ to bisanhydro-l-cystinyl-l-cystine,

[S·CH₂·CH<NH·CO>CH·CH₂·S]₂, decomp. (without melting) 250—310°, [α]_D²⁵ +312.5° in H₂O (mol. wt. determined), hydrolysed (conc. HCl) to an 89% yield of cystine. (I) with Et₂ glutamate gives Et₂ di(carbobenzyloxy)-l-cystyl-di-l-glutamate, m.p. 145°, converted by PH₄I into Et₂ cysteinylglutamate hydriodide; this with NH₃-EtOH at 0° gives a product which when aerated in H₂O containing NH₃ and FeCl₃ gives Et₂ anhydro-l-cystyl-di-l-γ-glutamate, m.p. 259°. Me₂ di(carbobenzyloxy)-l-cystyl-di-l-glutamate, m.p. 139°, similarly gives Me₂ anhydro-l-cystyl-di-l-γ-glutamate, m.p. 258°. Similarly Et₂ di(carbobenzyloxy)-l-cystyl-di-l-aspartate, m.p. 145°, gives Et anhydro-l-cystyl-di-l-β-aspartate, m.p. 246°, and Et₂ di(carbobenzyloxy)-l-cystyl-dityrosinate, m.p. 168—175°, gives anhydro-l-cystyl-di-l-tyrosine, m.p. 283° (decomp.). E. W. W.

Nitroso- and bromo-phenylpyriminazole. V. K. MATVEEV (Bull. Acad. Sci. U.R.S.S., 1936, 1005—1015).—3-Nitroso- (I), m.p. 163—164°, and 3-bromo-2-phenylpyriminazole (II), m.p. 129—130°,

prepared by the usual reactions, are described. Br and (I) yield (II). R. T.

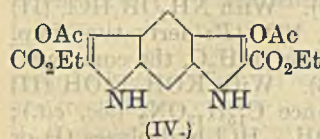
Metal carbonyls. XXIV, XXV. [Compounds of cobalt and nickel with o-phenanthroline and 2:2'-dipyridyl].—See A., I, 322.

Chemiluminescent organic compounds. IV. Amino- and hydrazino-cyclophthalhydrazides and their relative luminescent power. H. D. K. DREW and F. H. PEARMAN (J.C.S., 1937, 586—592).—3-Aminophthalimide with MeI-MeOH gives N-methyl-3-dimethylaminophthalimide methiodide, m.p. 204° (decomp.), from which MeI cannot be eliminated, and with Me₂SO₄ is obtained 3-methylaminophthalimide (I), m.p. 218° [3-N-Ac derivative, m.p. 285° (decomp.)]. This with 1 mol. of N₂H₄ forms N-amino-3-methylaminophthalimide, m.p. 194°, transformed above the m.p. into 5-methylaminophthalaz-1:4-dione, m.p. 331° (decomp.) [5-N-Ac derivative, m.p. 329° (decomp.)], also obtained from (I) and 3 mols. of N₂H₄. 3:6-Dichlorophthalimide with aq. NH₃ and Cu₂I₂ forms 3:6-diaminophthalimide (II), m.p. 298° (decomp.) [Ac₂ derivative, m.p. 321° (decomp.)], which with N₂H₄ in H₂O yields 3:6-diamino-N-amino-phthalimide, m.p. 282° (+H₂O), and in EtOH affords N-amino-3:6-diacetamidophthalimide, m.p. 319° (decomp.) (Ac derivative, m.p. 248°) N₂H₄ and (II) yield 5:8-diaminophthalaz-1:4-dione, m.p. 329° (decomp.) [+H₂O; Ac₂ derivative, m.p. 279° (decomp.); Ac₃ derivative, m.p. 306° (decomp.)]. (III) and NaOH, followed by HCl and Ac₂O, give 3:6-diacetamidophthalic anhydride, m.p. 279°. 4:5-Dichlorophthalimide, m.p. 221°, is obtained from the anhydride. 6:7-Dichlorophthalaz-1:4-dione, Cu₂I₂, and aq. NH₃ yield 6:7-diaminophthalaz-1:4-dione, m.p. 340° [+2H₂O; phenanthrazine derivative (+2H₂O, m.p. >340°)]. Na phthalimide-3-hydrazine-β-sulphonate (IV) is hydrolysed to 3-hydrazinophthalimide, m.p. 216° and 208°, converted by N₂H₄ into N-amino-3-hydrazinophthalimide, m.p. 202°. N₂H₄ and (IV) in EtOH form Na N-aminophthalimide-3-hydrazine-β-sulphonate, and in H₂O afford Na phthalaz-1:4-dione-5-hydrazone-β-sulphonate, hydrolysed to 5-hydrazinophthalaz-1:4-dione, m.p. 312° (decomp.). Pyromellitic dianhydride and N₂H₄ give pyromellitaz-1:4:6:9-tetraone [Na salt (+4H₂O)].

Fluorescence occurs in the phthalimides and cyclohydrazides containing NH₂ ortho to the junction of the rings, but not in those containing m-NH₂. The N-aminophthalimides derived from fluorescent phthalimides are non-fluorescent; this is not due to the removal of the imide-H, but is an effect of the N-NH₂ itself, since fluorescence persists in the N-methyl- and N-phenyl-phthalimides. The luminescent power of the substances described has been compared; only the phthalaz-1:4-diones show chemiluminescence, the 5-ring compounds giving no visible light in any instance. The open-chain hydrazides glow only when transformation into 6-ring hydrazides has taken place. F. R. S.

Heterocyclic compounds containing nitrogen. XXIX. Derivatives of m- and p-phenylenediamine and of 6-amino-oxindole. P. RUGGLI and R. GRAND (Helv. Chim. Acta, 1937, 20, 373—386; cf. this vol., 214).—m-C₆H₄(NH₂)₂ and CHBr(CO₂Et)₂

at room temp. give Et_2 *m*-phenylenediaminomalonate (I), m.p. 79°. Et_2 *p*-phenylenediaminomalonate (II), m.p. 108°, and Et_2 benzidinedimalonate (III), m.p. 134°, are obtained analogously. (I) loses EtOH at 205–220° and the product is acetylated to Et_2



3 : 5-diacetoxybenzodipyrrole-2 : 6-dicarboxylate (IV), m.p. 180°, which does not give an indigoid dye when melted with KOH; the yield is poor.

Attempted ring-closure with (II) or (III) gives only amorphous products. A ring-closure under milder conditions and from simpler reactants is illustrated by the production of Et 2 : 5-diketo-1 : 3-diphenyltetrahydroglyoxaline-4-carboxylate, m.p. 134.5°, from $PhNCO$ and $NHPh \cdot CH(CO_2Et)_2$ at 145°. *p*-Phenylenediglycine appears to yield polymerised products when treated successively with $SOCl_2$ and $AlCl_3$. $m\text{-}C_6H_4(NH_2)_2$ and CH_2BzBr in Et_2O -EtOH afford *di-m*-phenacylaminobenzene, m.p. 164°, in modest yield; it resinifies so readily that its prep. in quantity is difficult. *Di-p*-phenacylaminobenzene (V), m.p. (indef.) 151° (picrate, m.p. 124°; Ac_2 derivative, m.p. 227°), forms salts with acidic reagents (HCl -AcOH; conc. H_2SO_4) and does not yield cryst. compounds with the customary amine hydrochlorides. $m\text{-}NO_2 \cdot C_6H_4 \cdot NH_2$ and CH_2BzBr afford *m*-nitrophenacylaniline, m.p. 168°, which could not be cyclised. *p*-Acetamidophenacylaniline, m.p. 173°, from CH_2BzBr , $p\text{-}NH_2 \cdot C_6H_4 \cdot NHAc$, and Na_2CO_3 in EtOH at 50°, yields (V) when hydrolysed with AcOH and conc. HCl containing a little Zn dust and is cyclised by $p\text{-}NH_2 \cdot C_6H_4 \cdot NHAc \cdot HCl$ at 170–175° to 5-acetamido-2(or 3)-phenylindole, m.p. 217°. Et 2 : 4-dinitrophenylacetate, b.p. 200–210°/13 mm., is reduced (H_2 -Ni-EtOH-EtOAc- H_2O) to Et 2 : 4-diaminophenylacetate, m.p. 75° [Ac_2 , m.p. 190°, and Bz_2 , m.p. 161°, derivatives; picrate, decomp. (indef.) 165–215°]. Acidification and evaporation of the reduced solution gives 6-amino-oxindole hydrochloride in 78% yield, whence 6-amino-oxindole (VI), m.p. about 200° (decomp.). 6-*p*-Toluenesulphonamido-oxindole, m.p. 228–229°, is transformed by NaOH and Me_2SO_4 into *N*-methyl-6-*p*-toluenesulphonamido-oxindole, m.p. 253°, and ON-dimethyl-6-*p*-toluenesulphonamido-oxindole, m.p. 203°; the latter substance is hydrolysed by 80% H_2SO_4 at 135–150° to 5-amino-ON-dimethyloxindole, m.p. 165–166°, the *NO*-derivative, m.p. 137°, of which could not be reduced to the corresponding hydrazino-compound. (VI) is converted by $CH_2Cl \cdot COCl$ in Et_2O -dioxan at 0° into 6-chloroacetamido-oxindole, decomp. >270°, which is completely decomposed by $AlCl_3$ -NaCl at 170–190°. (VI) and Ac_2O in C_6H_6N afford 6-acetamido-oxindole, decomp. >335°, transformed by HNO_3 (d 1.51) at –12° to 0° into 5(?)-nitro-6-acetamido-oxindole, decomp. 250–300°, which does not give defined products when reduced, hydrolysed, and then treated with HCO_2H or AcOH.

H. W.

Preparation of 2-phenylpyriminazole. V. K. MATVEEV (Bull. Acad. Sci. U.R.S.S., 1936, 533–542; cf. Tschitschibabin, A., 1926, 1153).—2-Phenylpyriminazole (oxalate, decomp. at 195°; sulphate, m.p. 190°) is obtained in theoretical yield from 2-amino-

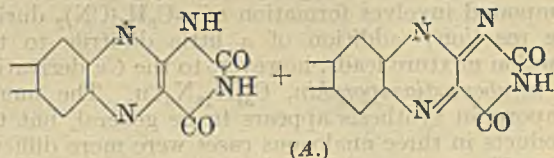
pyridine (I) and phenacyl chloride or bromide (II) in aq. $NaHCO_3$ at room temp.; the reaction is supposed to take place between the pyridonimine form of (I) and the enol form of (II).

R. T.

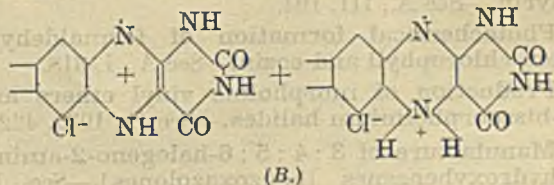
Lumazines and alloxazines. R. KUHN and A. H. COOK (Ber., 1937, 70, [B], 761–768).—The compound, $CH_3N \cdot C \cdot NH \cdot CO$ or $CH_3N \cdot C \cdot NH \cdot CO$, although previously designated alloxazine, is now termed lumazine (I) since the former nomenclature is now customary for the tricyclic system. Addition of a solution of trimeric glyoxal in warm H_2O to a hot aq. solution of 4 : 5-diamino-2 : 6-dihydroxypyrimidine sulphate (II) gives (I), m.p. >350°, which under the Hg-vapour lamp gives bluish-green, green, and blue fluorescence in neutral, alkaline, and acid solution, respectively. It is converted by CH_2N_2 into a yellow product which resinifies in air; 1 : 3-dimethyl-lumazine is not obtained from the Ag salt and MeI. Polymeric AcCHO and (II) give methyl-lumazine, m.p. >340°, probably a mixture of the 6- and 7-Me compounds, whilst 6 : 7-dimethyl-lumazine, m.p. >340°, is derived from (II) and Ac_2 . Condensation of *p*-benzoquinone with (II) could not be effected whereas β-naphthaquinone gives a mixture of the isomeric 1' : 2'-naphthalumazine-a (1 : 3- Me_2 derivative, m.p. 258–260°) and 1' : 2'-naphthalumazine-b, m.p. >330° [1 : 3- Me_2 derivative, m.p. 304° (decomp.)]. Phenanthraquinone and (II) afford 9' : 10'-phenanthralumazine (whence 1 : 3-dimethyl-5 : 6 : 7 : 8-dibenzalloxazine, m.p. 337°), also obtained from 9 : 10-diaminophenanthrene dihydrochloride and alloxan tetrahydrate (III) in dil. AcOH. 3 : 4-(NH_2) $_2$ $C_6H_3 \cdot CO_2H$ and (III) give a mixture of alloxazine-6- and -7-carboxylic acid, converted by CH_2N_2 into the Me_3 derivative-a, m.p. 165°, and Me_3 compound-b, m.p. 184°. Condensations with (II) can also be effected with benzil, dihydroxytartaric acid, isatin, and alloxan.

H. W.

Verdo-, chloro-, and rhodo-flavins. R. KUHN and R. STRÖBELE (Ber., 1937, 70, [B], 753–760).—6 : 7-Dimethyl-9-*l*-araboflavin (I) passes through three well-defined stages in its reduction to the leucoflavin

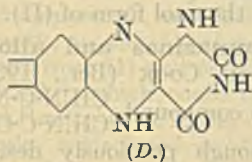
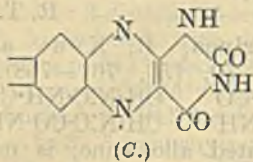


(II). Lactoflavin behaved similarly. The various products are almost instantaneously oxidised to (I) when shaken with O_2 , H_2O_2 being quantitatively produced. Verdo-6 : 7-dimethyl-9-*l*-araboflavin (III) is



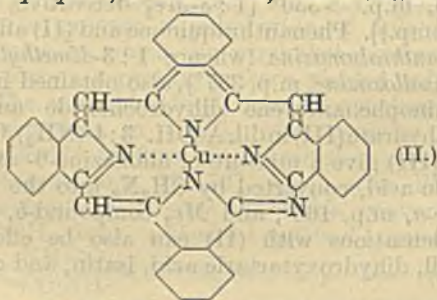
obtained as the Na salt when (I) in 0.1N-NaOH is catalytically hydrogenated or reduced with $Na_2S_2O_4$. It is brownish-green and since it is paramagnetic the

structure *A* is assigned to (III). In conc. HCl (III) dissolves to a blood-red solution of *rhodo-6:7-dimethyl-9-l-araboflavin*, isolated as the carmine-red



dihydrochloride (IV) of constitution *B*. When washed with H₂O in absence of air (IV) is hydrolysed to a very sensitive brown base, converted by air into grass-green *chloro-6:7-dimethyl-9-l-araboflavin*, probably *C*, predominatingly dimeric; the formulation with N^{II} is based on Wieland's observations on substituted hydrazines. For (II) the structure *D* is established by the isolation of monoacetyldihydro-compounds from various flavins. H. W.

Action of cuprous cyanide on *o*-halogeno-acetophenones. J. H. HELBERGER (Annalen, 1937, 529, 205—218).—2-Bromo-4-methylacetophenone, b.p. 130°/12 mm., is obtained from CH₃Ac·CO₂Et and 2:4-C₆H₃BrMe·COCl, and 1-chloro-2-acetylnaphthalene, m.p. 53°, b.p. 175°/12 mm., from 1:2-C₁₀H₆Cl·COCl. *o*-Bromo- or -chloro-acetophenone with CuCN in quinoline at 210—220° give the *Cu* derivative (II) of *tetrabenzozaporphin*, a violet salt, which sublimes at



>500°/vac., is very stable to H₂SO₄, gives *o*-C₆H₄(CO)₂O and *o*-C₆H₄(CO)₂NH with hot HNO₃, has a 6-banded absorption spectrum, and generally resembles the phthalocyanines. Formation of this compound involves formation of *o*-C₆H₄(CN)₂ during the reaction; addition of a little dinitrile to the reaction mixture leads, however, to the *Cu* derivative of *tetrabenzodiazaporphin*, C₃₄H₁₈N₆Cu. The monoazaporphin synthesis appears to be general, but the products in three analogous cases were more difficult to purify. R. S. C.

New blood-pigment: pseudo-methæmoglobin.—See A., III, 194.

Cytochrome-C. Synthesis from protoporphyrin.—See A., III, 194.

Photochemical formation of formaldehyde from chlorophyll and eosin.—See A., I, 318.

Production of morpholine vinyl ethers and *N*-bismorpholinium halides.—See B., 1937, 422.

Manufacture of 3:4:5:6-halogeno-2-amino-1-hydroxybenzenes [benzoxazolones].—See B., 1937, 420.

Action of semicarbazide hydrochloride on oximinotriphenylpyrrole. VI. T. AJELLO (Gaz-

zetta, 1937, 67, 55—68).—Oximinotriphenylpyrrole and semicarbazide hydrochloride yield the semicarbazone (I), m.p. 227°, of 3-benzoyl-4:5-diphenylisooxazole (II), m.p. 158°, together with (NH·CO·NH₂)₂, aminotriphenylpyrrole, and triphenylpyrrolylhydroxylamine (cf. this vol., 30). With NH₂OH·HCl, (II) gives an *oxime* (III), m.p. 162° (*Bz* derivative, m.p. 122°), or, on prolonged boiling in H₂O, the compound C₂₂H₁₆O₂N₂ (A., 1935, 763). With KOH·EtOH (II) or (III) forms the substance C₁₅H₁₂ON₂ (*loc. cit.*); with KOH, (II) gives BzOH. HCl hydrolyses (I) or (III) to (II). E. W. W.

Condensation of isatin with phenols. I. α -Naphthol. J. O. GABEL and V. M. ZUBAROVSKI (J. Gen. Chem. Russ., 1937, 7, 305—310).—Isatin and α -C₁₀H₇·OH at 110—120° in presence of POCl₃ yield 2-keto-3:3-bis- α -naphthoxyindoline (*Ac* derivative, m.p. 273°), whilst in AcOH at the b.p. the product is 2-keto-3-(3':4'-benzo-9'-xanthyl)indoline, m.p. 360° (*Ac* derivative, m.p. 305°). R. T.

Behaviour of ethyl thiazole-5-carboxylate methiodide on reduction. H. ERLENMEYER, A. EPRECHT, and H. VON MEYENBURG (Helv. Chim. Acta, 1937, 20, 514—515).—The substance, m.p. 153°, is unchanged by H₂ in PO₄''' solution (p_H 7.5) in presence of Pt-black at atm. pressure whereas Et nicotinate methiodide readily absorbs H₂ under these conditions. With Na₂S₂O₄—NaHCO₃ reaction is

$$\begin{array}{l} \text{C}(\text{CO}_2\text{Et})\text{CH} \\ \text{S} \text{---} \text{CH} \text{---} \text{NMe}^+ + \text{I}^- + 2\text{H}^+ \rightarrow \\ \text{C}(\text{CO}_2\text{Et})\text{CH} \\ \text{S} \text{---} \text{CH}_2 \text{---} \text{NMe} + \text{HI} \end{array}$$

H. W.

Thiazole and thiadiazine formation from thiosemicarbazones. J. McLEAN and F. J. WILSON (J.C.S., 1937, 556—559).—CH₂Cl·COMe (I) reacts with the Na salt of the appropriate thiosemicarbazone (PhCHO, COMe₂, and CPhMe, respectively) to give 2-keto-4-methyl-2:3-dihydrothiazole-2-benzylidene-, m.p. 190° (*hydrochloride*, m.p. 131°), -isopropylidene-, m.p. 90° or 115°, and - α -phenylethylidene-hydrazone, m.p. 134° (*hydrochloride*, m.p. 154°). Hydrolysis of these compounds with 0.1*N*-HCl yields 2-keto-4-methyl-2:3-dihydrothiazole-2-hydrazone, isolated as the *picrate*, m.p. 192°, and with conc. HCl forms 2-amino-5-methyl-1:3:4-thiadiazine hydrochloride, m.p. 228° (*picrolonate*, m.p. 235°). The corresponding base, m.p. 109°, is obtained from (I) and thiosemicarbazide, forms *Ac*₃, m.p. 167°, and *Bz*₂ derivatives, m.p. 201—202°, and reacts with CS₂ and PhNCS to yield respectively 2-amino-5-methyl-1:3:4-thiadiazine 5-methyl-1:3:4-thiadiazine-2-dithiocarbamate, decomp. 142°, and 2-aminothioformamido-5-methyl-1:3:4-thiadiazine, m.p. 200° (decomp.). CH₂Cl·CHO with acetone- and benzaldehyde-thiosemicarbazone affords respectively 2-keto-2:3-dihydrothiazole-2-isopropylidene-, m.p. 140°, and -benzylidene-hydrazone, m.p. 169°. F. R. S.

Rings containing nitrogen and sulphur. H. WUYTS (Bull. Soc. chim. Belg., 1937, 46, 27—45).—A review of recent work on the carbodithioic acids, R·CS₂H, and the prep. from them of aromatic aldehydes, tetrazines, indole derivatives, thio- and glycothio-diazolines. A. LI.

Recent work in alkaloid chemistry. A. P. OREKHOV (Bull. Acad. Sci. U.R.S.S., 1936, 935—955).—A lecture. R. T.

Tobacco alkaloids. XII. Occurrence of *dl*-nornicotine, *dl*-anatabine, and *l*-anabasine in tobacco. E. SPÄTH and F. KESZTLER (Ber., 1937, 70, [B], 704—709).—The mother-liquors from the prep. of *l*-nornicotine (I) diperchlorate (A., 1935, 1387) are freed by successive use of *l*- and *d*-6:6'-dinitro-2:2'-diphenic acid from the optically active isomerides as far as possible and an optically inactive product is obtained by suitable admixture of the feebly active bases derived from the respective salts. This gives a homogeneous, optically inactive 2:4-dinitrobenzoyl derivative, m.p. 159—160°, identical with that derived from 2:4-(NO₂)₂C₆H₃·COCl and authentic *dl*-nornicotine (II). Since (I) is not readily racemised it is probable that (II) exists pre-formed in tobacco and is not formed by racemisation of (I) during extraction. A sample of German tobacco contained almost exclusively optically homogeneous (I) whereas *d*-nornicotine from Australian *Duboisia Hopwoodii*, Muell. is more than half racemised.

Crystallisation of the diperchlorate of crude *l*-anatabine from H₂O leads to the isolation of *dl*-anatabine perchlorate, m.p. 129—130° (corresponding dipicrate, m.p. 201—201.5°; trinitro-*m*-tolylxide, m.p. 140—141°; dipicolonate, m.p. 233—235°). The constitution of the free base (III) is established by its dehydrogenation to 2:3'-dipyridyl, by the oxidation of its Bz derivative to BzOH, nicotinic and hippuric acid, and by its resolution into its optical antipodes. Since (III) is racemised with difficulty, it probably exists pre-formed in the plant. The isolation of *l*-anabasine, identical with that obtained from *Anabasis aphylla*, from the mother-liquors from (III) is described. H. W.

Alkaloids of *Salsola richteri*. A. P. OREKHOV and N. F. PROSKURNINA (Bull. Acad. Sci. U.R.S.S., 1936, 957—960).—Salsolidine, [α]_D²⁰ —53°, is the O-Me ether of *l*-salsoline, [α]_D²⁰ —44°. R. T.

Alkaloids of different varieties of *Senecio*. R. A. KONOVALOVA (Bull. Acad. Sci. U.R.S.S., 1936, 961—967).—Platyphylline, from *S. platyphyllus*, is hydrolysed to platynecinic acid and platynecine, C₈H₁₃N(OH)₂, the dichloride of which is hydrolysed to heliotridane. R. T.

Alkaloids of *Senecio*. III. Jacobine, jacobine, and jaconine. G. BARGER and J. J. BLACKIE (J.C.S., 1937, 584—586).—Jacobine (nitrate, m.p. 234°, [α]_D²⁰ —28.6° in H₂O) is the principal alkaloid of *Senecio* (cf. Manske, A., 1932, 286); it is hydrolysed to retronecine and jaconecic acid. From material collected in June and July, but not in that in August, jacobine, C₁₈H₂₅O₅N, m.p. 217°, [α]_D²⁰ —109.6° in CHCl₃ (nitrate, m.p. 215°, [α]_D²⁰ —77.4° in H₂O), and jaconine, C₁₈H₂₅O₈N·H₂O, m.p. 146°, have been isolated. F. R. S.

Synthesis of cocaine from hyoscyamine. M. N. SCHTSCHUKINA, R. A. LAPINA, and N. A. PREOBRAZHENSKI (Bull. Acad. Sci. U.R.S.S., 1936, 997—1004).—See A., 1936, 1131. Hyoscyamine and H₂O (5 hr. at the b.p.) give tropine in 88.5% yield. R. T.

M.p. of cocaine hydrochloride. A. L. DRAGANESCO (J. Pharm. Chim., 1937, [viii], 25, 389—391).—The m.p. (to clear liquid) varies from 179° (heated during 60 min.) to 186.5° (26 min.), being 182—183° if the bath is kept const. at 170° and then heated at 2° per min. A. Li.

Constituents of *Lunasia costulata*. H. DIETTERLE and H. BEYL (Arch. Pharm., 1937, 275, 276).—Lunacrine is C₁₆H₁₉O₃N (cf. this vol., 216). R. S. C.

Roots of *Aristolochia indica*, Linn. III. Isolation of the alkaloid aristolochine. P. R. KRISHNASWAMY and B. L. MANJUNATH (J. Indian Chem. Soc., 1937, 14, 39—41).—Aristolochine (A., 1935, 1433) is C₁₇H₁₉O₃N and has [α]_D²⁵ —268.6° [in MeOH?]; it contains OMe and NMe₂. With PhMe and C₆H₆, it gives additive compounds (cf. loc. cit.), m.p. 159° (decomp.), and 163° (decomp.), respectively, both decomposed by MeOH. Its hydrochloride has [α]_D²⁵ —236.2°; the hydrobromide, m.p. 262°, picrate, decomp. 222°, and picrolonate, m.p. 232° (decomp.) are prepared. E. W. W.

Alkaloids of fumariaceous plants. XII. *Corydalis scouleri*, Hk. XIII. *Corydalis sibirica*, Pers. R. H. F. MANSKE (Canad. J. Res., 1936, 14, B, 347—353, 354—359).—XII. The following alkaloids are isolated (see A., 1933, 728) from the whole plant *C. scouleri*, Hk.: protopine (I) (0.15%), cryptopine (II) (0.004%) α-allo-cryptopine (0.001%), bicuculline (III) (0.20%), scoulerine (IV) (0.06%), capnoidine (0.12%) (A., 1933, 841), corlumine (V) (0.12%) and corluminine (0.02%) (this vol., 80), alkaloid-η (0.002%), C₂₁H₂₁O₆N, m.p. 180°, probably isomeric with adlumine and (V), and alkaloid-θ (VI) (0.002%), C₁₆H₁₇O₃N, m.p. 183° (methylation product, m.p. 162°).

XIII. From *C. sibirica*, Pers., are isolated (I) (0.47%), (III) (0.10%), traces of (II), (IV), (V), and (VI), three new non-phenolic alkaloids, alkaloid-κ C₁₉H₁₇O₅N + MeOH, m.p. 139° [hydrochloride, sinters 238—242°, m.p. 247° (decomp.)], -λ, C₁₉H₁₉O₅N, m.p. 212°, and -μ, C₁₈H₁₇O₅N, m.p. 236°, the last two each containing 2 OMe; and a phenolic alkaloid-ι, C₂₁H₂₁O₄N, m.p. 248°, containing 1 OMe. All m.p. are corr. J. W. B.

Isomerism of norcoralydine. G. HAHN and W. KLEY (Ber., 1937, 70, [B], 685—688).—The discrepancies between the observations of Pictet and Chou (A., 1916, i, 418) and Späth and Kruta (A., 1929, 201) are explained by the observation that norcoralydine exists in an α-form, m.p. 146° (hydrochloride, m.p. 218—220°; orange-red picrate, m.p. 138—140°), and a β-variety, m.p. 158° (hydrochloride, m.p. 213°; pale-yellow picrate, m.p. 109—110°). The forms do not differ greatly in stability since either form may separate from hot EtOH or Et₂O. Isolation of pure forms can be effected only by microscopical observation of the process of crystallisation with removal of the crystals at a suitable instant. H. W.

Narcotoline, a new alkaloid of the poppy (*Papaver somniferum*). F. WRENDE (Arch. exp. Path. Pharm., 1937, 184, 331—335).—Narcotoline,

Organo-arsenic compounds. P. S. YANG (Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 4, 1—8).—A review. J. D. R.

Arsinated derivatives of mixed ketones. (Miss) R. E. OMER and C. S. HAMILTON (J. Amer. Chem. Soc., 1937, 59, 642—644).—Resorcinol and PrCN give (Hoesch) a 65% yield of 2:4-dihydroxypropio-phenone and thence the *Me*₂ ether, m.p. 67°, *Ac*₂, m.p. 89°, and 5-*NO*₂-derivative, m.p. 131° (*Me*₂ ether, m.p. 177°), and 5-amino-2:4-dihydroxypropio-phenone, m.p. 147—151° (decomp.) (*Me*₂ ether, m.p. 107°). 5-Nitro-, m.p. 142°, and 5-amino-2:4-dihydroxyacetophenone, m.p. 137—142° (decomp.) (*Me*₂ ether, m.p. 114°), are similarly prepared. The amine hydrochlorides have m.p. >300°. The dihydroxyamino-ketones give very poor, the dimethoxyaminoketones good, yields of 2:4-dimethoxy-5-arsino-acetophenone, m.p. 250°, and -propio-phenone, m.p. 243°.

R. S. C.

Structure and toxicity of arsinic acids of the diphenylamine series. V. A. ISMAILSKI and A. M. SIMONOV (J. Gen. Chem. Russ., 1937, 7, 499—507).—The following substituted nitro- and amino-diphenylamine-4-arsinic acids have been prepared by the reactions: $\text{NH}_2\text{R} + 4\text{-chloro-3-nitrophenylarsinic acid} + \text{NaOH} \rightarrow \text{R}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{AsO}_3\text{H}_2 \rightarrow (+\text{Na}_2\text{S}_2\text{O}_4) \text{R}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{AsO}_3\text{H}_2$: 3'-acetamido-, 3'-hydroxy-, 2'- and 3'-methoxy-, 4'-ethoxy-, 2-nitro-4'-p-aminophenyl-, and 3'-acetamido-, 4'-hydroxy-, and 4'-ethoxy-2-amino-diphenylamine-4-arsinic acid. Lowering of toxicity and intensification of colour are greater when R is in the 3' than in the 4' position.

R. T.

Colour of 2-nitrodiphenylamine-4-arsinic acid derivatives containing additional auxo-groups. I. Auxo-enoid systems separated from the chromophore. V. A. ISMAILSKI and A. M. SIMONOV (J. Gen. Chem. Russ., 1937, 7, 508—512; cf. preceding abstract).—The influence of substituents on the colour of diphenylamine-4-arsinic acid derivatives is discussed.

R. T.

Diarsyls. VIII. Amino- and hydroxy-diarsyls. F. F. BLIGKE and G. L. WEBSTER (J. Amer. Chem. Soc., 1937, 59, 537—539).—2:2'-Diaminotetraphenylarsyl oxide (I) and *o*-aminodiphenylarsine, b.p. 218—220°/35 mm. (from *o*-aminodiphenylarsinic acid, Hg-Zn dust, and aq. HCl), in EtOH and N₂ give 2:2'-diaminotetraphenylarsyl, m.p. 133—135°, also obtained together with (AsPh₂)₂ from (I) and AsHPh₂, which absorbs O₂ readily in PhBr. 3:3'-Diaminotetraphenylarsyl oxide and 50% H₃PO₂ + a little HI afford 3:3'-diaminotetraphenylarsyl, m.p. 146—148°. *m*-Hydroxydiphenylarsinic acid and H₃PO₂ similarly give 3:3'-dihydroxytetraphenylarsyl, m.p. 134—136°, methylated (*Me*₂SO₄, aq. NaOH) to the 3:3'-(*OMe*)₂-derivative, m.p. 98—99°. These diarsyls react readily with O₂ in C₆H₅Me. 3:3'-Diamino-4:4'-dihydroxydiphenyldimethyldiarsyl, m.p. 184—185° (dihydrochloride, m.p. 168—170°), is prepared from 3-amino-4-hydroxyphenylmethylarsinic acid and H₃PO₂ (cf. Berthelm, A., 1915, i, 331). *o*-Methoxydiphenyliodoarsine reacts rapidly with mol. Ag in C₆H₆ to give the oily diarsyl. All m.p. are in sealed tubes in N₂.

H. B.

Tetra-arylphosphonium chlorides. N. N. MELNIKOV, A. E. KRETOV, and B. I. MELTZER (J. Gen. Chem. Russ., 1937, 7, 461—463).—PPh₃ and CH₂RX in C₆H₆ at the b.p. yield the following phosphonium salts, of the general formula PPh₃RX: X = Cl, R = Ac, m.p. 234° (decomp.); X = Br, R = Ac, m.p. 221°; X = Br, R = Bz, m.p. 253° (decomp.); X = Cl, R = *o*-, m.p. 230° (decomp.), *m*-, m.p. 247° (decomp.), and *p*-C₆H₄·NO₂, m.p. 247° (decomp.); X = Cl, R = *p*-C₆H₄·CN, m.p. 244—245°.

R. T.

2:6-Diselena-4-spiroheptane and other selena-cyclobutanes. H. J. BACKER and H. J. WINTER (Rec. trav. chim., 1937, 56, 492—509).—K₂Se (I) and C(CH₂Br)₄ in EtOH-C₆H₆ give 2:6-diselena-4-spiroheptane, m.p. 67° (mercurichloride; tetraiodide, [unstable]), which, with MeI affords 3-iodomethyl-3-methylselenolmethyl-1-selenacyclobutane methiodide $\text{Se} \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}_2\text{I} \\ \text{CH}_2\text{SeMe}_3\text{I} \end{smallmatrix}$ m.p. 112—113° (picrate, m.p. 113—113.5°). CMe₂(CH₂Br)₂ with (I) in EtOH yields 3:3-dimethyl-1-selenacyclobutane (II), b.p. 56°/40 mm. [di-iodide (unstable); mercuri-chloride and -iodide], which, with MeI yields dimethyl-γ-iodo-ββ-dimethylpropylselenonium iodide, m.p. 105° [platinichloride, m.p. 167°; aurichloride, m.p. 98°; picrate, m.p. 114.5—115°]. Br or Cl₂ converts (II) into γ-bromo-ββ-dimethylpropylselenium tribromide, m.p. 103° (decomp.), and γ-chloro-ββ-dimethylpropylselenium trichloride, m.p. 100° (decomp.), respectively, converted by AgOH into γ-bromo-, m.p. 91°, and γ-chloro-ββ-dimethylpropylselenious acid (III), m.p. 90—91°. Oxidation (H₂O₂) of (II) affords 3:3-dimethyl-1-selenacyclobutane 1:1-dioxide, m.p. 132—132.5°, also obtained from the Na salt of (III) in EtOH. cycloHexanone with Na and CH₂Cl·CO₂Et in EtOH afford γ-pentamethylene-βγ-epoxyethylpropionate, b.p. 126°/15 mm., hydrolysed (NaOH) to the acid, which with HCl yields hexahydrobenzaldehyde; this with CH₂O yields 1:1-bishydroxymethylcyclohexane (improved method), converted by PBr₃ into 1:1-bisbromomethylcyclohexane (IV), b.p. 139.5°/17 mm. With (I) in EtOH, (IV) affords 2-selena-4-spiro-nonane (V), b.p. 103.5—104°/13 mm., m.p. -46° (mercuri-chloride and -bromide), which with MeI affords γ-iodo-β-pentamethylenepropylselenonium iodide (picrate, m.p. 121—121.5°). (V) in AcOH with I yields 2:2-di-iodo-2-selena-4-spiro-nonane, m.p. 59° (decomp.), and with Br in CCl₄, 1-bromomethyl-1-tribromoselenium-methylcyclohexane, m.p. 121—122° (decomp.), converted by AgOH into γ-bromo-ββ-pentamethylenepropylselenious acid, m.p. 102.5—103°, the Na salt of which in EtOH affords 2-selena-4-spiro-nonane 2:2-dioxide, m.p. 50—55°. With Cl₂ in CCl₄, (V) gives 1-chloromethyl-1-trichloroselenium-methylcyclohexane, m.p. 102—104°, converted by AgOH into γ-chloro-ββ-pentamethylenepropylselenious acid, m.p. 100—100.5° (decomp.).

J. D. R.

Synthetic immunochemistry. I. Synthesis of *O*-β-glucosidotyrosine and its introduction into the protein molecule. R. F. CLUTTON, C. R. HARRINGTON, and T. H. MEAD (Biochem. J., 1937, 31, 764—771).—An attempt is made to prepare an

artificial compound antigen in which the carbohydrate group is attached to the protein through a naturally occurring type of chemical linking. *O*- β -*Glucosidotyrosine* (I), m.p. 282° (decomp.), $[\alpha]_{5181}^{20} -77^\circ$, is prepared by condensing acetobromoglucose with *N*-carbobenzyloxytyrosine Et ester, hydrolysis of the formed *O*-*tetra*-*acetyl*- β -*glucosido*-*N*-*carbobenzyl*-*oxytyrosine Et ester* (II), m.p. 108°, with $\text{Ba}(\text{OH})_2$ giving *O*- β -*glucosido*-*N*-*carbobenzyl*-*oxytyrosine*, m.p. 177°, $[\alpha]_{\text{D}}^{20} -24.2^\circ$, and subsequent reduction with Pd-H_2 . Emulsin hydrolyses (I). The *hydrazide* of (II) has m.p. 215°, $[\alpha]_{\text{D}}^{20} -37.5^\circ$, and when treated with HNO_2 yielded the *azide* and this was then coupled directly with gelatin (III) in alkaline solution to give *O*- β -*glucosido*-*N*-*carbobenzyl*-*oxytyrosylgelatin*. The carbobenzyloxy-groups were removed by treating the solution in anhyd. liquid NH_3 containing NH_4OAc with Na. Electrometric titration showed that no appreciable degradation of (III) had occurred. *O*- β -*Glucosidotyrosylgelatin* contained 4.6% of glucose and evidence is presented that in it the glucosido-tyrosine residues are attached to the $\alpha\text{-NH}_2$ -groups of the (III). P. W. C.

Structure of proteins. IV. **Benzoylated protein.**—See A., III, 245.

Microchemical contributions [to qualitative analysis]. XIV.—See A., I, 326.

Manometric method for enzymic determination of arginine.—See A., III, 139.

Microdetermination of rubidium and caesium in organic compounds. H. ROTH (Mikrochem., 1937, 21, 227—230).—The material is evaporated down with H_2SO_4 , and Rb and Cs are finally weighed as sulphates. J. S. A.

Determination of nitrogen in diazo-compounds. H. ROTH (Mikrochem., Molisch Festschr., 1936, 375—378).—Certain diazo-compounds (*e.g.*, the diazo-ketones of unsaturated acids) are decomposed catalytically by CuO at room temp., thus giving low vals. for N. Such materials are weighed in a Sn foil capsule, which is embedded in the CuO tube filling. J. S. A.

(A) **Use of liquid amalgams for analysis of hydroxy-nitro-compounds.** M. I. PERRIER and M. M. LOBUNETZ. (B) **Determination of dinitrobenzene.** M. M. LOBUNETZ. (C) **Determination of nitro-group of nitrobenzene.** M. I. PERRIER and M. M. LOBUNETZ. (D) **Analysis of nitrosalicylic acid.** M. M. LOBUNETZ (Bull. Sci. Univ. Kiev, 1936, 2, 45—50, 69—72, 73—79, 81—83).—(A) 0.6—0.8 g. of *p*-nitrophenol in 4*N*-HCl is reduced by Zn-Hg to *p*-nitroaniline, which is titrated with 0.2*N*- NaNO_2 .

(B) 15 c.c. of Zn-Hg are added to 0.3—0.4 g. of $\text{C}_6\text{H}_4(\text{NO}_2)_2$ in MeOH, followed by 40 c.c. of 4*N*-HCl, the mixture is shaken, and the aq. $\text{C}_6\text{H}_4(\text{NH}_2)_2$ is diluted to 200 c.c. 1 g. of KBr, 25 c.c. of 0.2*N*-KBrO₃, and 5 c.c. of 4*N*-HCl are added to 25 c.c. of solution, the mixture is shaken, and 8 c.c. of 40% KI are added after 15 min. The I liberated is titrated with $\text{Na}_2\text{S}_2\text{O}_3$.

(C) PhNO_2 is determined analogously to $\text{C}_6\text{H}_4(\text{NO}_2)_2$.

(D) Nitrosalicylic acid is determined analogously to nitrophenol. R. T.

Detection of ethylvanillin (bourbonal). P. STADLER and K. WAGNER (Z. anal. Chem., 1937, 108, 161—167).—The blue coloration given by ethylvanillin (I) with FeCl_3 , unlike that given by vanillin (II), changes to a green colour at 60°. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + \text{HCl}$ gives ppts. of characteristic cryst. form with (I) and (II), that from (II) being luminescent in ultra-violet light. $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH}_2$ also gives characteristic ppts. (I), but not (II), gives a white ppt. when boiled with $\text{NaNO}_2 + \text{HNO}_3$. (I) when present alone may be determined by the gravimetric, volumetric, and colorimetric methods applicable for (II). J. S. A.

Determination of benzoic acid. F. W. EDWARDS, H. R. NANJI, and M. K. HASSAN (Analyst, 1937, 62, 172—177).—Nicholls' method (A., 1928, 313) is modified, notably to avoid the necessity for controlled acidity, by extracting the salicylic acid (I) formed in Et_2O and determining it colorimetrically with FeCl_3 . The Jorissen test as modified by Nicholls (*loc. cit.*) is preferred for the determination of (I) in admixture with BzOH, whilst BzOH is detected by the Illing-Mohler test (A., 1932, 632) and determined by Nicholls' method after selective oxidation of (I) by alkaline KMnO_4 and extraction in Et_2O (*cf.* following abstract). J. G.

Detection and determination of *p*-hydroxybenzoic acid and its derivatives, with special reference to their distinction from salicylic and benzoic acids. F. W. EDWARDS, H. R. NANJI, and M. K. HASSAN (Analyst, 1937, 62, 178—185).—The NH_4 salts of the acids are obtained after extraction with Et_2O and hydrolysis of esters with KOH in EtOH, and a scheme is provided enabling the acids to be identified from the results obtained with the Millon, FeCl_3 , Jorissen, Cu salt, Nicholls, and Illing-Mohler tests (*cf.* preceding abstract). $p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ is determined colorimetrically, using Millon's reagent; in presence of salicylic acid the shade must be matched against that given by one of a series of mixtures of the two acids. Procedures for dealing with cordials, fatty foods, and meat and fish products are described. J. G.

Solubility of semicarbazones in dilute hydrochloric acid.—See A., I, 298.

2 : 3 : 7-Trihydroxy-9-methyl-6-fluorone, special reagent for antimony cations.—See A., I, 330.

Identification of different barbituric acids with Millon's reagent. M. PAGET and TILLY (J. Pharm. Chim., 1937, [viii], 25, 222—223).—The characteristic reactions of ten substituted barbituric acids with Millon's agent are tabulated. E. H. S.

Functional chemistry of morphine. New colour reaction for morphine and its pseudolic derivatives. J. A. SANCHEZ (J. Pharm. Chim., 1937, [viii], 25, 346—351).—All derivatives with *sec.* alcohol group in ring 1 of Gulland and Robinson's formula, but no others, give a stable red-violet colour on boiling the solid with vanillin-HCl solution. R. M. M. O.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1937.



New electronic theory of organic reactions. H. F. TSEOU (Separate, Hanchow, 223 pp.; cf. A., 1936, 960).—An extension of previous theory and a survey of the literature of theory of org. reactions. The position of an element in the periodic table is determined by the condition of the electrons in the outermost sphere and there is an equilibrium point at which the electrons of an element would have no tendency to be displaced either inwards or outwards. C is supposed to be an element slightly to the left of this point but its position may be moved either farther to the right or left depending on whether it is joined to an element which repels electrons strongly or to one which attracts them. In doubly and trebly bound C and also in cyclic compounds the octets of electrons are more compact. In every chemical reaction there is involved a complicated system of electron displacements of the reacting mols., and the at. radius of an element can by no means be a const. quantity but is different in different compounds. With this formulation the facts in org. chemistry are accounted for. The theory finds substantial proofs in different physical measurements. F. R. S.

Catalytic isomerisation of *n*-hexene and octene in presence of zinc chloride and phosphoric acid. A. D. PETROV and M. A. TSCHELZOVA (Compt. rend. Acad. Sci. U.R.S.S., 1937, 15, 79—84).—Branched-chain hydrocarbons containing a quaternary C are much less readily chlorinated by SbCl_5 in CHCl_3 than those with only *tert.* C (cf. A., 1935, 1102). In absence of CHCl_3 , chlorination is much more extensive. Octan- β -ol when heated with ZnCl_2 affords a mixture of Δ^2 - (I) and Δ^3 -octene (II), which when heated at 325—350° for 25 hr. in presence of ZnCl_2 and then hydrogenated affords 12% of *iso*-compounds (III). Higher yields of (III) are obtained at pressures of 50 atm. and in <1.5 hr. in presence of ZnCl_2 or H_3PO_4 . (I) and (II), individually, similarly afford isomerides hydrogenated to products containing 46.8% of (III). Δ^2 -Hexene after isomerisation and hydrogenation gives 23% of (III). J. L. D.

Completion of Krafft's proof of the structure of cetene. S. L. LANGEDIJK and P. L. STEDEHOUDER (Rec. trav. chim., 1937, 56, 526—528).—Cetene is Δ^2 -*n*-hexadecene since its dibromide (I) is converted by 0.9*N*-EtOH-KOH at 180—200° first into Δ^2 -*n*-hexadecene (II) (ppt. with AgNO_3 -EtOH), isomerised by prolonged treatment into Δ^8 -*n*-hexadecene (III) (no Ag compound). (III) is unchanged by solid KOH at 190°/75 mm., conditions under which (I) affords (II). J. W. B.

Determination of the constitution of hydrocarbons of the $\text{C}_n\text{H}_{2n-2}$ series. A. E. FAVORSKI

and M. D. BONE (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 499—504).—Oxidation of allene hydrocarbons with KMnO_4 yields unsaturated glycols which isomerise at once to ketols, which are further oxidised to acids, giving no differentiation between the acetylenic and allene type. With O_3 , diozonides are formed which decompose to CO_2 and dicarboxylic acids, from the nature of which the structure of the allene may be deduced. J. D. R.

Characteristics of hydrocarbons of the $\text{C}_n\text{H}_{2n-4}$ series with conjugated double and triple linkings. A. I. ZACHAROVA (Sci. Rep. Leningrad State Univ., 1936, 2, No. 2, 162—195).—COMeEt is added gradually to a suspension of KOH in Et_2O saturated with C_2H_2 at -10° , C_2H_2 is passed for 8 hr., and H_2O is added, when $\text{OH}\cdot\text{CMeEt}\cdot\text{C}\cdot\text{CH}$ is obtained in 70% yield. This gives $\text{CHMe}\cdot\text{CMe}\cdot\text{C}\cdot\text{CH}$ (I) when passed over MgSO_4 at 230°. (I) and KOH in MeOH (120°; 12 hr.) give β -methoxy- γ -methyl- Δ^2 -pentadiene (II), b.p. 45—46°/15 mm., converted by heating with 1% H_2SO_4 (25—30°; 8 hr.) into $\text{CHMe}\cdot\text{CMe}\cdot\text{COMe}$, and by O_3 in CHCl_3 into MeCHO , AcCO_2Me , and HCO_2H . (I) and KOH in EtOH yield similarly β -ethoxy- γ -methyl- Δ^2 -pentadiene (III), b.p. 54—55°/15 mm., which reacts analogously to (I) with 1% H_2SO_4 , and gives β -ethoxy- γ -methylpentane, b.p. 140—142°, on hydrogenation (Pd-Ni). A dimeride of (I), b.p. 74—75°/10 mm., is obtained as a by-product of the prep. of (II) or (III); it yields $\text{H}_2\text{C}_2\text{O}_4$, COMeEt, and AcOH with KMnO_4 , and is probably $(\text{CMeEt}\cdot\text{C}\cdot\text{C})_2$. R. T.

Photochemical oxidation, sensitised by bromine, of carbon tetrabromide to carbonyl bromide and bromine in solution in carbon tetrachloride. W. KOBLITZ, H. MEISSNER, and H. J. SCHUMACHER (Ber., 1937, 70, [B], 1080—1086).—The rate of Br-sensitised photochemical oxidation of CBr_4 in CCl_4 has been examined by measurement of the O_2 absorbed at 14° and 0.3° with light of λ 436 m μ . With relatively high [Br] the complete change may be nearly represented by $2\text{CBr}_4 + \text{O}_2 = 2\text{COBr}_2 + 2\text{Br}_2$. Even with high $[\text{CBr}_4]$ the quantum yield of the change is <1 mol. per *h*v. Br is feebly restrictive, O_2 weakly accelerating, to the change. COBr_2 has no influence. The temp. coeff. between 0° and 14° is about 1.2 per 10°. The course of the change is approx. expressed, $QA = [\text{CBr}_4]/0.11 + 0.06[\text{Br}_2]/[\text{O}_2] + [\text{CBr}_4]$. The energy required to separate the first Br from CBr_4 is >50 kg.-cal. H. W.

Halogenation of ethylenes. I. ROBERTS and G. E. KIMBALL (J. Amer. Chem. Soc., 1937, 59, 947—948).—Contrary to usual statements, free rotation about the C:C linking is not to be expected in

CRR'Hal·CR''R'''. Since the ionisation potentials of C and halogen are similar, an equally probable structure is $\text{Hal}^+ \left\langle \begin{smallmatrix} \text{CRR}' \\ \text{CR}''\text{R}'' \end{smallmatrix} \right\rangle$, in which the halogen acts as donor of two electrons to form a co-ordinate link with the C; the actual structure of the ion is intermediate between the two. Reaction of an ethylene with halogen involves first formation of such an ion, which then adds Hal⁻ by a "three-atom" reaction; this gives *trans* addition. If, however, R and R'' are similarly charged, e.g., CO₂⁻, the force of repulsion may suffice to cause rotation before the second step of addition occurs; this leads to *cis* addition. This mechanism is shown to accord with experiment.

R. S. C.

Addition of hydrogen bromide to allyl bromide in the presence of various substances. VI. Homogeneity of the catalytic action of oxygen. Theory of the oxygen effect. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1937, 12, 173—176).—CH₂:CH·CH₂Br and HBr react in the presence of O₂ in an identical manner and to the same extent whatever is the surface area at which reaction occurs. It is suggested as an interpretation of earlier results (cf. this vol., 224) that O₂ catalyses the formation of CH₂(CH₂Br)₂ and not CHMeBr·CH₂Br in the above reaction.

J. L. D.

Preparation of aliphatic dihalogeno-compounds of high mol. wt. J. VON BRAUN and E. KAMP (Ber., 1937, 70, [B], 973—978).—The prep. of long-chained dihalogeno-paraffins according to the scheme, Br[CH₂]_n·Br → OPh[CH₂]_n·Br → OPh[CH₂]_{2n}·OPh → Hal[CH₂]_{2n}·Hal fails when *n* is large owing to the difficulty of the final step. This difficulty disappears when the corresponding alkyl ethers are used but the b.p. of Br[CH₂]_n·Br and OAlk[CH₂]₂·Br are inconveniently close; it is completely avoided by use of hydroaromatic ethers. CH₂(CH₂·CH₂·OPh)₂ is reduced (Ni) by H₂ at about 200°/100 atm. to *α*-dicyclohexyloxypentane (I), b.p. 180—184°/10 mm., with some cyclohexyloxypentane and cyclohexanol (II). (I) and fuming HBr at 100° yield Br[CH₂]₁₅·Br and cyclohexyl bromide. OPh[CH₂]₁₀·OPh, b.p. 215—225°/0.05 mm., best obtained from OH[CH₂]₁₀·OH, is hydrogenated to *α*-dicyclohexyloxydecane (III), b.p. 168—170°/0.05 mm., mixed with *n*-decane, (II), and cyclohexyl decyl ether. (III) gives Br[CH₂]₁₀·Br (IV), m.p. 28°. (IV) and NaOPh in EtOH give unchanged material, OPh[CH₂]₁₀·OPh, and OPh[CH₂]₁₀·Br; the latter is converted by Na in Et₂O into Ph decyl ether, *κ*-phenoxy-Δ⁹-decene, and diphenoxyeicosane, m.p. 92—93°, from which impure dibromoeicosane is isolated.

H. W.

1:2- and 1:4-Addition. II. Nitrogen tetroxide and trimethylethylene [*iso*amylene]. A. MICHAEL and G. H. CARLSON (J. Amer. Chem. Soc., 1937, 59, 843—849; cf. this vol., 244).—N₂O₄, alone or in light petroleum, functions as O·NO₂ + NO, since with CMe₂·CHMe it gives 43.2—47.6 and 35.2—39.2%, respectively, of bis(*iso*amylene nitrosate) (I). In Et₂O it functions mainly as O·NO + NO₂, since in this solvent it yields about 35% of *γ*-nitro-β-methylbutan-β-ol nitrite (II), m.p. 60°, and 0.15—8.2% of

(I). In both cases the yields are relatively independent of temp. and thus of the equilibrium, N₂O₄ ⇌ 2NO₂. In neither case could the other products be identified. As usually obtained, (I) is blue; distillation in steam gives a colourless product, removing about 25% of a blue oil, b.p. 43—47°/2 mm. (C 48.72, H 7.25, N 12.58%), which is not the monomeric form of (I). (I) is identified by reaction with NaSPh and NaSEt in EtOH to give NaNO₃ and the *thio*-ethers, NO·CHMe·CMe₂·SR, R = Ph, m.p. 90° (PhNCO additive compound, m.p. 113—114°), and Et, m.p. 60° (PhNCO additive compound, m.p. 122°), respectively. (II) and NaSPh in EtOH give the *thio*-ether, NO₂·CHMe·CMe₂·SPh, an oil, stable to H₂O₂—AcOH, but oxidised by CrO₃ to the *sulphone*, m.p. 102—103°.

R. S. C.

Catalytic oxidation of organic compounds by carbon dioxide. I. Oxidation of *iso*amyl alcohol in presence of oxide and salt catalysts. A. M. RUBINSTEIN, K. P. PREOBRAZHENSKAJA, and L. S. TSCHERNOMORSKAJA. II. Oxidation of different alcohols. A. M. RUBINSTEIN and N. F. LUKASCHINA. III. Mechanism of oxidation of alcohols. A. M. RUBINSTEIN and N. M. NAGIEV (Sci. Rep. Moscow State Univ., 1936, No. 6, 287—297, 299—305, 307—319).—I. The yields of CH₃Pr^β·CHO (I) and CH₃Pr^β·CO₂H (II) obtained under optimum conditions by passing *iso*-C₅H₁₁·OH (III) in a stream of CO₂ over a no. of catalysts are: U₃O₈ at 450°, 72.9 and 12.3, MoO₃-pumice at 450° 59.3, and 18.2, Ca(VO₃)₂ (IV) at 600°, 58.6 and 3.7, Sn(VO₃)₂ at 450°, 56 and 30.4, and MoO₃-V₂O₅-pumice at 400°, 40.8 and 37.9%. Except in the case of (IV) the optimum temp. are the same as for oxidation by air in presence of the same catalysts. The optimum rates of flow of CO₂ are determined for each catalyst.

II. (III)-CO₂ mixtures yield chiefly CH₃:CHPr^β (V) in presence of V₂O₅ at 550°, and Bu^βOH-CO₂ mixtures give chiefly CH₃:CMe₂ with MoO₃ at 350—500°. CH₃Ph·OH and CO₂ afford PhCHO 54% and BzOH 32.5% with MoO₃ at 400°.

III. The gaseous products obtained by passing (III), (III)-H₂O, (III)-CO₂, or (III)-CO₂-H₂O mixtures over MoO₃-asbestos at 350—500° contain chiefly H₂, together with (V), CO, and CO₂, the yield of (V) being greatest, and of H₂ least, when (III) alone is passed over the catalyst. The ratio (I)/(II) in the liquid product falls with increasing temp. Under the conditions of the experiment, HCO₂H (VI) yields CO and H₂. The reaction of oxidation of alcohols by CO₂ is represented: CH₂R·OH + CO₂ → R·CHO + (VI); (VI) → CO + H₂; R·CHO + H₂O → CHR(OH)₂ → R·CO₂H + H₂; CHR(OH)₂ + CO₂ → R·CO₂H + (VI).

R. T.

Photochemical peroxide formation. VIII. Oxidation of glycol by molecular oxygen in ultra-violet light. IX. Oxidation of paracet-aldehyde by molecular oxygen in ultra-violet light. R. CANTIENI (Z. wiss. Phot., 1937, 36, 116—118, 119—120).—VIII. (CH₂·OH)₂ forms a peroxide OH·CH₂·CH₂·O₂H with O₂ in ultra-violet light. Further action of the peroxide with activated (CH₂·OH)₂ gives CO₂, H₂O, and (CH₂·OH)₂. The reaction is similar to the photochemical oxidation of glycerol (A., 1936, 1091).

IX. Paracetaldehyde forms a peroxide when mixed with O_2 and exposed to ultra-violet light. The amount of peroxide produced varies linearly with time at first, but later decreases owing to decomp.

A. J. M.

Acidimetric determination of glycerol (and erythritol) by periodates. M. L. MALAPRADE (Bull. Soc. chim., 1937, [v], 4, 906—910).—The solution is neutralised to Me-red, treated with an excess of $NaIO_4$ for 20 min. and then with conc. aq. KNO_3 (which ppts. KIO_4). The liberated HCO_2H ($2NaIO_4 + C_3H_8O_3 \rightarrow 2CH_2O + HCO_2H + 2NaIO_3 + H_2O$) is determined by titration with a strong base. With KIO_4 the procedure is simpler. The method is exact in presence of $EtOH$ or $(CH_2OH)_2$. Weak bases and acids weaker than HCO_2H must be absent, but strong bases and acids do not interfere provided that they have no reducing or pptg. action towards $NaIO_4$. Under similar conditions erythritol affords $2HCO_2H$.

H. W.

Synthesis of ethyl isobutyl ether. E. M. MARKS, D. LIPKIN, and B. BETTMAN (J. Amer. Chem. Soc., 1937, 59, 946—947).— $EtOBu^i$ is obtained in 70% yield from dry Bu^iOH , Na, and Et_2SO_4 at 120—130°. Use of KOH instead of Na gives a 22.5% yield; 50% aq. KOH gives no ether. $OEtCHMeEt$ is obtained in 48% yield by use of Na.

R. S. C.

Oxidation of ethyl mercaptan and ethyl disulphide by bromine in the presence of water. H. A. YOUNG (J. Amer. Chem. Soc., 1937, 59, 811—812).—The following reactions are proved to occur in CCl_4-H_2O mixtures: $EtSH + 3Br_2 + 3H_2O \rightarrow EtSO_3H + 6HBr$; $Et_2S_2 + 5Br_2 + 6H_2O \rightarrow 2EtSO_3H + 10HBr$. Br vapour very rapidly oxidises $EtSH$ to Et_2S_2 .

R. S. C.

Rate of oxidation of ethyl disulphide by bromine. H. A. YOUNG and M. B. YOUNG (J. Amer. Chem. Soc., 1937, 59, 812—816).— Et_2S_2 removes Br or I from the aq. layer of CCl_4-H_2O mixtures, indicating complex formation, but the reaction is reversible. A kinetic study shows that the initial rate of reaction is given by $dBr_2/dt = k \times [Et_2S_2](Br_2)_2$, k being dependent on the rate of shaking. It is suggested that the first steps are: (fast) $Et_2S_2 + 2Br_2 \rightarrow 2EtSBr_2$; (slow) $EtSBr_2 + H_2O \rightarrow EtSO + 2H^+ + 2Br^-$, followed by formation of $EtSO_2Br$ and $EtSO_3H$. The reaction is catalysed by H^+ ; when $EtSH$ reacts with Br, the first reaction is formation of Et_2S_2 and HBr , and subsequent reaction is, therefore, abnormally fast.

R. S. C.

Formation of organo-metalloidal and similar compounds by micro-organisms. V. Methylated alkyl sulphides. Fission of the disulphide link. F. CHALLENGER and A. A. RAWLINGS (J.C.S., 1937, 868—875).—The prep. of the following reference substances is described: *MeSEt dimercurichloride*, m.p. 127—128°; *benzylmethylthiylsulphonium picrate*, m.p. 100.5—101°; *MeSPr^a mercurichloride*, m.p. 163.5—165°; *benzylmethyl-n-propylsulphonium picrate*, m.p. 95—95.5°; *MeSEt platinochloride*, m.p. 121.5—122.5°. When $(EtS)_2$ is treated with excess of saturated aq. $HgCl_2$, 70% yields of $SEt \cdot HgCl \cdot HgCl_2$ (I), m.p. 151°, and with $(Pr^a S)_2$ $SPr^a \cdot HgCl \cdot HgCl_2$, m.p.

139°, are obtained, the products being identical with those from the corresponding mercaptans. With $EtSH$ and $HgCl_2$, $(EtS)_2Hg$, m.p. 76—77°, $SEt \cdot HgCl$, m.p. $\pm 260^\circ$, and (I) may be obtained at will and with Pr^aSH the corresponding compounds, m.p. 65—66°, 182°, and 138—139°, respectively. Neither $SR \cdot HgCl \cdot HgCl_2$ nor $SR \cdot HgCl$ liberates any mercaptan when warmed with $NaOH$ in an air stream. When $(EtS)_2$, $(Pr^a S)_2$, $EtSH$, and Pr^aSH are added to cultures of *Penicillium brevicaulis* (*Scopulariopsis brevicaulis*), Saccardo, and the gases produced are absorbed in $HgCl_2$, ppts. are obtained which on treatment with $NaOH$ in a stream of air yield $MeSEt$ and $MeSPr^a$. Negative results were obtained when $(PhS)_2$ and $(CH_2Ph \cdot S)_2$ were added to the cultures.

P. W. C.

Determination of $\beta\beta$ -dichlorodiethyl sulphide. L. BURUANA (Z. anal. Chem., 1937, 109, 107—110).— $(C_2H_4Cl)_2S$ in $EtOH$ is pptd. by 5 parts of 24% aq. Na_2HgI_4 at 30—40°. The oily ppt. is collected by centrifuging in a graduated tube, and its vol. is measured. Hydrolysis products are not pptd. by Na_2HgI_4 .

J. S. A.

Unsaturated sulphides derived from the chloroethylenes. N. W. CUSA and H. MCCOMBIE (J.C.S., 1937, 767—770).— $NaSPh$ with $(CHCl)_2$ in $EtOH$ affords *diphenylthioethylene*, b.p. 235—242°/760 mm., m.p. 62°. $(CH_2Cl \cdot CHCl)_2S$ when distilled at ordinary pressure yields *dichlorodivinyl sulphide* (I), b.p. 75—80°/15 mm., converted by $NaSPh$ in $EtOH$ into *di(phenylthiol)divinyl sulphide* (II), m.p. 78°, converted by $NaOEt$ into an isomeride of (II), m.p. 138°. (I) with $\beta-C_{10}H_7 \cdot OH$ and Na in $EtOH$ yields *di-(β -naphthylthio)divinyl sulphide*, m.p. 151—152°. C_2HCl_3 with $NaSPh$ in $EtOH$ affords *Ph $\alpha\beta$ -dichlorovinyl sulphide* (III), b.p. 145—150°/22 mm., converted by $NaOMe$ into *Ph α -chloro- β (?)methoxyvinyl sulphide*, b.p. 160—165°/20 mm., by Cl_2 in CCl_4 into *Ph $\alpha\alpha\beta\beta$ -tetrachloroethyl sulphide*, b.p. 175—182°/20 mm., and by $NaOH$ in aq. $EtOH$ into $NaSPh$ and glycolic acid. C_2HCl_3 with $NaSEt$ in $EtOH$ affords mixtures of *Et dichlorovinyl sulphide*, b.p. 77—80°/30 mm., with *chlorodi(ethylthiol)ethylene* and *tri(ethylthiol)ethylene*. $NaSPh$ with C_2Cl_4 in $EtOH$ yields *s-dichlorodiphenylthioethylene*, m.p. 71—72°, the Cl of which is very resistant to further substitution. $SNa \cdot C_2H_4 \cdot OH$ and C_2Cl_4 in $EtOH$, followed by treatment with $SOCl_2$, afford isomeric compounds, $C_6H_5Cl_3S_2$, (a) b.p. 145—147°/30 mm., and (b) m.p. 72—73°.

J. D. R.

Enzymic ester syntheses.—See A., III, 269.

Constitution of peptides. I. Structure of organic acids. Raman bands of the acidic function in acids and their derivatives. C. SANNIÉ and U. POREMSKI (Bull. Soc. chim., 1937, [v], 4, 880—893).—Comparison of the Raman spectra of aldehydes, ketones, and esters with those of acids, homogeneous or dissolved in non-polar solvents, shows that the band at 1730 cm^{-1} attributed to the double linking $C=O$ appears in acids at 1650 cm^{-1} . This is not due to a displacement such as is frequently caused by substitution and the phenomenon can be explained only by the existence of two different forms of acids. The same doubling is observed in solutions of acids in

polar solvents, the relative intensity of the two bands being a function of the concn. of acid. The two forms of the acid are thus in an equilibrium dependent on the polarity of the solvent, the concn., and the temp. Since the mol. associations of acids also depend on these factors it is reasonable to attribute 1650 to the existence of associated mols. The frequency appears to be due to the vibration of a system of 2 atoms rather than to that of the entire complex or of the group O-C-O. 1650 may therefore be due to C:O deformed by the production of particular linkings of the type of the "H bond" of Latimer and Rodebush between doubly linked O and OH of the CO_2H of the associated mol. or to the existence of a "H bond" itself. Association of acids is comparable with the phenomena of "chelate structure" by which the infrared and Raman spectra of aldehydes, *o*-hydroxybenzoic acids, and OH-acids are explained. In all these cases the internuclear distances of the O atoms (2.65 Å.) are very close and appear to justify such a view.

H. W.

Rates of reaction of aliphatic acid halides. R. LEIMU (Ber., 1937, 70, [B], 1040—1053).—Among fatty acid halides AcCl reacts most rapidly and EtCOCl least rapidly with $\text{CH}_3\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ (I), $\text{CH}_3\text{Ph}\cdot\text{OH}$ (II), or cyclohexanol (III) in dioxan. Higher chlorides are somewhat less active than AcCl . The rate of alcoholysis corresponds with the strength of the α -acids, but this does not appear to be a general regularity. Branching in the C chain, particularly at $\text{C}_{\alpha\alpha}$, greatly diminishes the rate of reaction with (I) but the effect is much less obvious with (II) or (III). With alkoxyacetyl chlorides the rate of reaction has a relative minimum when O is in the β -position to CO. Similar regularities are observed in the behaviour of chlorides of Cl-acids, the rates for the α -, β -, and γ -derivatives being about = 20 : 2 : 3. The α -compounds are characterised by high rate of reaction and small temp. coeff. which diminishes as the rate of reaction increases. The greater rate is connected with a smaller energy of activation of alcoholysis. The theory of induced alternating polarities cannot be used in explanation of the behaviour of fatty acid chlorides towards alcohols. COCl_2 is characterised by a very high rate of alcoholysis and its relatively low temp. coeff. ClCO_2Et reacts so slowly with (I) in dioxan that the rate cannot be measured satisfactorily. ClCO_2Et and ClCO_2Pr^a react at about the same rate with MeOH , ClCO_2Me more and ClCO_2Pr^b much less rapidly. The greatest rate is observed with $\text{ClCO}_2\text{CH}_2\cdot\text{CH}_2\text{Cl}$. AcBr and (I) react very rapidly and the change has a small temp. coeff. The following new or revised data are recorded for various chlorides: dl- α -methylbutyryl, b.p. 118.0—118.3°/761 mm.; β -methylbutyryl, b.p. 117.8°/766 mm.; $\text{CCl}_3\cdot\text{COCl}$, b.p. 117.9°/754 mm., from $\text{CCl}_3\cdot\text{CO}_2\text{H}$ and SOCl_2 in C_6H_6 ; dl- α -chloropropionyl, b.p. 110.7—111.2°/760 mm.; α -dichloro-, b.p. 117.4—117.8°/753 mm.; dl- α - β -dichloro-, b.p. 43—44°/10 mm., and β - β -dichloro-, b.p. 43—44°/10 mm.; -propionyl; γ -chlorobutyryl, b.p. 35—36°/12 mm.; methoxy-, b.p. 50—51°/69 mm.; ethoxy-, b.p. 49—50°/37 mm., and n-propoxy-, b.p. 44—44.5°/12.5 mm.; acetyl-; β -methoxy-, b.p. 27—27.5°/3 mm., and β -ethoxy-, b.p. 28—28.5°/2 mm.; -propionyl; γ -methoxy-, b.p. 46—47°/7 mm., and γ -ethoxy-, b.p. 35°/10 mm.; -butyryl; δ -methoxy-,

b.p. 51—51.5°/3 mm., and δ -ethoxy-, b.p. 64—66°/4 mm., -valeryl.

H. W.

Kinetics of thermal decomposition of potassium formate. A. A. BALANDIN, L. C. FREIDLIN, and D. N. VASKEVITSCH (Sci. Rep. Moscow State Univ., 1936, No. 6, 321—345).— HCO_2K (I) yields chiefly K_2CO_3 (II) at 370—425°, and chiefly $\text{K}_2\text{C}_2\text{O}_4$ (III) at 440—475°; both reactions proceed simultaneously at 425—440°. The energy of activation of the former reaction is 10 times that of the latter. The ratio (II)/(III) of the product falls when <27% of glass is added to the (I), and then rises rapidly to a max. for 10 : 1 glass-(I) mixtures, at 440°; the ratio is at a min. for 0.8 : 10 (III)-(I), or 3 : 10 (II)-(I) mixtures, at 405°. The process is represented as $2(\text{I}) \rightarrow \text{OH}\cdot\text{CH}(\text{OK})\cdot\text{CO}_2\text{K}$ (IV) \rightarrow (III) + H_2 ; (IV) \rightarrow (II) + CH_2O ; $\text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2$.

R. T.

Alkylacetylenes and their addition compounds. XX. Reactions of alkenyl esters derived from alkylacetylenes. S. J. SLANINA and G. F. HENNION (J. Amer. Chem. Soc., 1937, 59, 855—857; cf. A., 1936, 1490).—Esters, $\text{RCO}_2\text{CR}'\text{CH}_2$, are readily cleaved by various reagents to the ketone, COMeR , and appropriate second fragment. β -Acetoxy- Δ^a -heptene (I) with HBr at 0° gives an unstable additive compound, yielding AcBr , AcOH , $\text{COMe}\cdot\text{C}_5\text{H}_{11}$, and a substance, b.p. 140—150°/23 mm.; β -acetoxy- Δ^a -hexene (II) gives AcBr , COMeBu , and a substance, b.p. 130—140°/23 mm. β -Chloroacetoxy- Δ^a -hexene and HCl at 10° give $\text{CH}_2\text{Cl}\cdot\text{COCl}$ and COMeBu . With NaOMe or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ in NaOH (I) yields MeOAc and $\text{COMe}\cdot\text{C}_5\text{H}_{11}$, and with Na in liquid NH_3 gives $\text{COMe}\cdot\text{C}_5\text{H}_{11}$, but it is stable for 1 hr. in liquid NH_3 alone at -34° . With I in liquid NH_3 (II) gives CHI_3 .

R. S. C.

Preparation of angelic acid. H. P. KAUFMANN and K. KÜCHLER (Ber., 1937, 70, [B], 915—916).—Tiglic acid (I) is converted into its dibromide and thence into β -bromoangelic acid. This is debrominated in neutral or acid solution to (I), whereas in alkaline solution, particularly with Na-Hg , it affords angelic acid in 70% yield.

H. W.

Geometrical isomerism of halogen substituted ethylenic acids. II. Addition of hydrogen bromide to tetrolic acid. V. O. MOCHNATSKH and A. I. STOLIAROV (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 559—564).— $\text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{H}$ with aq. HBr (saturated at 0°) at 25° or at 40° affords a mixture of α - β -dibromobutyric acids but aq. HBr (saturated at 25°) at 18—20° gives a mixture of β -bromocrotonic acids separated by fractional crystallisation from H_2O into the β -bromocrotonic acid, m.p. 94.4° (*Na* and *Ca* salts), and, from the mother-liquor, its stereoisomeric form, m.p. 80—81° (*Ca* salt).

J. W. B.

n-Fatty acids and certain of their derivatives.—See A., I, 289.

Fats. XXXV. Diene synthesis with fats. IV. Determination of the diene value by iodometry. Diene values of various fats and their interpretation. H. P. KAUFMANN, J. BALTES, and H. BÜTER (Ber., 1937, 70, [B], 903—907; cf. A., 1936, 966).—Maleic anhydride (I) can be determined in COMe_2 or

in solvents not miscible with H_2O by addition of $KI-KIO_3$ and an excess of $0.1N-Na_2S_2O_3$; after 2 hr. $0.1N-I = 0.1N-Na_2S_2O_3$ is added and the liberated I is titrated with $0.1N-Na_2S_2O_3$. The method is applied to the determination of the "diene val." of fats, which is more accurate when effected in sealed vessels than under a reflux condenser; the presence of the additive products and of other components of the fat is immaterial. The examples of Δ^9 -octadecadienoic acid and α -elaeostearic acid are cited. The "diene val." is an excellent method for the determination of the content in oils of acids with conjugated double linkings but several oils have "diene vals." although, as far as is known, they are not derived from such acids. The possibility of re-esterification of (I) appears excluded and it must therefore be assumed that all oils which have a diene val. contain compounds which can react with (I). The free fatty acids derived from such oils have no diene vals. so that either the unsaponifiable matter is responsible for the action or the diene-fatty acids are changed under the mildest conditions of hydrolysis. Experiments with linseed oil suggest the presence of previously unrecognised, unsaturated compounds of very labile nature. H. W.

Catalysed polymerisation in monolayers of drying oils.—See A., I, 369.

Action of periodic acid on lactic and pyruvic acid. P. FLEURY and (Mlle.) S. BOISSON (Compt. rend., 1937, 204, 1264—1266; cf. A., 1933, 376).— $0.05-0.025N$ -Lactic acid (I) with HIO_4 ($0.4-0.1N$) during 1 hr. at 100° affords $MeCO$ (1 mol.), CO_2 , and H_2O following the reduction of 1 mol. of HIO_4 . (I) is very slowly oxidised completely but the amount of aldehyde present decreases only slowly, because CH_2O is formed by the action of hot HIO_4 on $MeOH$, a secondary product of the main reaction. $AcCO_2H$ with hot HIO_4 easily affords $AcOH$, which resists further oxidation. J. L. D.

Determination of lactic acid in presence of methylglyoxal. E. BAUER and F. ZIEGLER (Z. physiol. Chem., 1937, 247, 1—5).—To the mixture of lactic acid (I) and $AcCHO$ (II) containing H_2SO_4 and $MnSO_4$ a tenfold excess of H_2O_2 is added to destroy (II); the mixture is boiled for 20 min., most of the excess of H_2O_2 is destroyed with $KMnO_4$ or $NaHSO_3$, and (I) is determined by titration with $0.01N-I$ in the usual way. With biological material the method is best applied after deproteinisation. W. McC.

Oxidation of some polyhydroxylic and polyetherlyenic higher fatty acids by aqueous alkaline permanganate solutions. T. G. GREEN and T. P. HILDITCH (J.C.S., 1937, 764—767).—With $KMnO_4$ in aq. $NaOH$, the isomeric pairs of θ -dihydroxy-stearic and -palmitic acids afford suberic acid (I); ε -dihydroxystearic acid yields undecic and glutaric acid, whilst the isomeric μ -dihydroxybehenic acids yield decane- $\alpha\omega$ -dicarboxylic acid. Similarly, θ - μ -tetra- and θ - μ - μ -hexahydroxystearic acids afford (I) and azelaic acid, also formed from α - and β -elaeostearic acids. J. D. R.

Diels-Alder diene synthesis. R. DELABY (Bull. Soc. chim., 1937, [v], 4, 765—791).—A lecture.

Dieneometry and the diene value of fats. H. P. KAUFMANN (Ber., 1937, 70, [B], 900—902).—The procedure of Ellis and Jones (B., 1937, 152) has no advantage over that of the author (A., 1936, 966) and the term "M.A. val." has no advantage over "diene val." H. W.

Halogenometric determination of fumaric acid. E. SZEGEDY (Z. anal. Chem., 1937, 109, 95—107).—An aq. solution of fumaric acid, free from other substances and exactly neutralised (phenolphthalein), is treated in a stoppered flask with an excess of $0.1N-Br$ in $N-KBr$. After 2 hr. in the dark, KI in $0.1N-HCl$ is added, and the liberated I is titrated with $Na_2S_2O_3$. Sources of error in the bromometric titration are discussed. J. S. A.

Contact isomerisation of methyl maleate. R. J. LEVINA (Sci. Rep. Moscow State Univ., 1934, No. 3, 183—185).— Me_2 maleate is converted into Me_2 fumarate by passing over Pd -asbestos at $205-206^\circ$ in CO_2 . R. T.

Structure of glutaconic acids and esters. IX. α -Methyl- and α -ethyl-glutaconic acids. F. S. FITZGERALD and G. A. R. KON (J.C.S., 1937, 725—727).—*trans*- α -Methyl- Δ^2 -propene- $\alpha\gamma$ -dicarboxylic acid (I) with $AcCl$ at 110° followed by hydration (cold H_2O) yields *cis*- α -methyl- Δ^2 -propene- $\alpha\gamma$ -dicarboxylic acid (II), m.p. $125-126^\circ$ (Me_2 ester, b.p. $82-85^\circ/2$ mm.). (I) in $EtOAc$ with O_3 affords $H_2C_2O_4$ and Me α -formylpropionate, whilst (II) gives $AcCO_2Me$. Similarly, *trans*- α -ethyl- Δ^2 -propene- $\alpha\gamma$ -dicarboxylic acid gives a non-homogeneous *cis*-acid, $H_2C_2O_4$ being the only identifiable product from O_3 on both the *cis*- and *trans*-acids in $EtOAc$. J. D. R.

Vinylene homologues of glutaconic acid. C. GRUNDMANN (Ber., 1937, 70, [B], 1148—1153).—Oxalocrotonic acid is converted by warm 3% H_2O_2 into glutaconic acid (yield 75%). Similar treatment of oxalosorbic acid (I) gives $\Delta^{2,7}$ -pentadiene- $\alpha\epsilon$ -dicarboxylic acid (Me_2 ester, b.p. $120-122^\circ/2$ mm., m.p. $39-40^\circ$), identical with the piperylenedicarboxylic acid obtained by Willstätter by degradation of the tropine alkaloids. Treatment of (I) with excess of H_2O_2 in alkaline solution leads to *trans-trans*-muconic acid. Condensation of the higher polyenedicarboxylic esters with $Et_2C_2O_4$ is greatly improved by use of $KOEt$ and C_5H_5N in the complete absence of moisture. The esters are hydrolysed by $2N-NaOH$ and $MeOH$ under N_2 at room temp. The following substances are thus obtained: *oxalo-octatrienoic acid*, m.p. $>360^\circ$ after much softening at $230-240^\circ$, oxidised to $\Delta^{2,7}$ -heptatriene- $\alpha\gamma$ -dicarboxylic acid, m.p. 199° ; *oxalodecatetraenoic acid*, m.p. $>360^\circ$ after softening at 250° , oxidised to $\Delta^{2,7,9}$ -nonatetraene- α -dicarboxylic acid, m.p. 215° when rapidly heated, m.p. $>360^\circ$ after gradual softening when heated slowly. H. W.

dl- and active methyldiglycollic acids and their derivatives. M. GODCHOT and P. VIELES (Bull. Soc. chim., 1937, [v], 4, 937—944; cf. A., 1936, 823).— Et_2 methyldiglycolate (Et α -carbethoxymethoxypropionate) of whatever degree of optical activity (dependent on that of the technical Et lactate used in its prep.) is transformed by NH_3-H_2O at 0° into *dl*-methyldiglycolldiamide (I), m.p. 126° (*Hg* deriv-

ative), which cannot be resolved into its optical antipodes by spontaneous crystallisation. (I) is hydrolysed by 10% NaOH to *dl*-methylidiglycollic acid, m.p. 61° (in sealed capillary) (*anhydride*,

$\text{O} \begin{array}{c} \text{CHMe-CO} \\ \text{CH}_2\text{-CO} \end{array} \text{O}$, b.p. 118°/28 mm.; *dianilide*, m.p. 92°).

H. W.

Catalytic oxidation of ascorbic acid.—See A., I, 368.

Vitamin-C [and scorbamic acid]. F. MICHEEL and R. MITTAG (Z. physiol. Chem., 1937, 247, 34—42; cf. this vol., 180).—Scorbamic acid (I), decomp. about 100°, yields with air, and especially with benzoquinone, a red dye catalytically reduced by H₂ to a colourless leuco-compound but not to (I). The dye is probably produced by irreversible condensation of 1 mol. of (I) with 1 mol. of dehydroscorbamic acid. Improved methods of preparing aminotetronic acid and 2-deoxy-*l*-ascorbic acid are described. W. McC.

Isomerisation of 2:3-dimethylascorbic acid. W. N. HAWORTH, E. L. HIRST, F. SMITH, and W. J. WILSON (J.C.S., 1937, 829—834).—Dimethylascorbic acid (I) with aq. Ba(OH)₂ isomerises to *isodimethylascorbic acid* (II), b.p. 175°(bath)/0.03 mm., $[\alpha]_D^{22}$ —18° in MeOH, showing no selective absorption, and converted quantitatively into the amide of (I), from which (II) may be regenerated by aq. Ba(OH)₂. (II) when heated at 120°/0.1 mm. yields in some cases (catalytic impurity) (I), whilst heating with MeOH-HCl affords 2-methylascorbic acid (III), a syrup, $[\alpha]_D^{20}$ +10° in H₂O, converted by CH₂N₂ into 2:3-dimethyl-*l*-ascorbic acid monohydrate (IV). *l*-Ascorbic acid (V) with CH₂N₂-Et₂O affords mainly 3-methylascorbic acid, but also small quantities of monomethylhetero-ascorbic acid (?1-methyl) (VI), formerly (cf. A., 1934, 1333) described as 2-methylascorbic acid, hydrolysed by H₂O to (V), and converted by CH₂N₂ into a Me₂ derivative which with H₂O yields (III). (I) with CPh₃Cl in C₅H₅N affords 6-triphenylmethyl-2:3-dimethyl-*l*-ascorbic acid (VII), m.p. 156°, $[\alpha]_D^{20}$ +35° in CHCl₃, and an isomeric substance (VIII), m.p. 178°, $[\alpha]_D^{20}$ +31° in CHCl₃, also produced by isomerisation of (VII) with MeOH-NH₃. (VII) and (VIII) with HCl-CHCl₃ yield (IV), with MeI-MeOH-Ag₂O give triphenylmethyltrimethyl-*l*-ascorbic acid, m.p. 131°, $[\alpha]_D^{20}$ +31.5° in CHCl₃, and with HCl-CHCl₃ at —5° give 2:3:5-trimethyl-*l*-ascorbic acid (IX), m.p. 69—70°, $[\alpha]_D^{20}$ —11.4° in H₂O (*mono-p*-nitrobenzoate, m.p. 118°), isomerised by Ba(OH)₂ to isotrimethyl-*l*-ascorbic acid (X), b.p. 115° (bath)/0.01 mm., m.p. 38°, $[\alpha]_D^{20}$ —34.9° in H₂O (*amide*, m.p. 115°, $[\alpha]_D^{20}$ —35.4°), showing no selective absorption in H₂O. When boiled with MeOH-HCl, (X) affords (III), methylated by CH₂N₂ to (IX). J. D. R.

Acetone derivatives of gluconic acid. W. N. HAWORTH, E. L. HIRST, and K. A. CHAMBERLAIN (J.C.S., 1937, 795—797).—Ca gluconate H₂SO₄, COMe₂, and CuSO₄ afford a mixture of *di*- (I), m.p. 154°, $[\alpha]_D^{20}$ +11° in EtOH, and *tri-isopropylidene-gluconic acid* (II), m.p. 111°, $[\alpha]_D^{20}$ +31° in EtOH, hydrolysed (MeOH-HCl) to (I). (I) with MeI-Ag₂O in MeOH yields *Me* 2-methyldiisopropylidenegluconate, b.p. 105°/0.02 mm., m.p. 44°, $[\alpha]_D^{20}$ +41° in H₂O,

which is hydrolysed (HCl) to 2-methyl- γ -gluconolactone, a syrup, $[\alpha]_D^{20}$ +45°, converted by MeOH-NH₃ into 2-methylgluconamide, m.p. 139°, $[\alpha]_D^{20}$ +39° in H₂O. X-Ray examination of (II) shows it to be probably either the 1:2, 3:4, 5:6- or the 1:2, 3:5, 4:6-[CMe₂]₃ compound. J. D. R.

alloMucic acid. F. L. HUMOLLER and W. F. McMANUS (J. Amer. Chem. Soc., 1937, 59, 945—946).—Priority of Posternak (A., 1936, 55) for the prep. of this acid is acknowledged (cf. this vol., 49).

R. S. C.

Constitution and reactions of thiocarbonyl tetrachloride. III. Reaction with primary alkylamines and phenols. J. M. CONNOLLY and G. M. DYSON (J.C.S., 1937, 827—828).—*n*-Heptyl- and allyl-amine in Et₂O with K₂CO₃ in H₂O and CSCI₄ in Et₂O afford respectively *S*-*n*-heptyl- and *S*-*n*-allyl-aminotrichloromethylthiol, both oils, decomp. 170°. NH₂R with CSCI₄ in ligroin yields NHR·S·CCl₃, converted by excess of NH₂R and HCl into NR·C(NHR)₂·HCl, also prepared by methylation (Me₂SO₄) of CS(NHR)₂ followed by heating with NH₂R. Thus are prepared triallyl-, m.p. 176°, tribenzyl-, m.p. 201°, and triisooamyl-, m.p. 206°, -guanidine hydrochloride. OPh·S·CCl₃ with NaOEt in EtOH affords *S*-ethoxytrichloromethylthiol, b.p. 155° (decomp.), also prepared from CSCI₄ and NaOEt in Et₂O-EtOH, converted by excess of NaOEt into Et₄ orthocarbonate, b.p. 158°. Similarly are prepared *S*-isobutoxytrichloromethylthiol, b.p. 181° (decomp.), and Bu₄ orthocarbonate, b.p. 238°.

J. D. R.

Thetines and selenetines. E. BILMANN and K. A. JENSEN (Bull. Soc. chim., 1936, [v], 3, 2310—2318).—CHMeBr·CO₂Et (I) when treated with Me₂S in the hot or cold yields SMe₂Br, m.p. 201—202° (sealed tube; cf. lit.), and *Et* α -methylthiopropionate (II), b.p. 173—175°/773 mm. and 70—72°/14 mm., also obtained from (I) and a suspension of NaSMe in Et₂O. The prep. of solid NaSMe by treatment of NaOEt-EtOH with MeSH and then Et₂O is described. (II) when treated with MeI in the hot or cold yields SMe₂I, m.p. 213—214° (sealed tube; cf. lit.), and CHMeI·CO₂Et. CHMeBr·CO₂H (III) with Et₂S in the cold during 17 days gives diethylpropiothetine hydrobromide, CHMe(SET₂)Br·CO₂H, m.p. 105—105.5° (decomp.), but with Me₂S (or Et₂S) at 100° SMe₂Br (or SET₂Br) and SMe·CHMe·CO₂H. Similarly, (I) and Me₂Se gives trimethylselenonium bromide, m.p. 197—198° (sealed tube). (III) with R₂Se (R = Me or Et) gives mixtures of CHMe(SeR₂)Br·CO₂H and SeR₃Br. All attempts to prepare propiothetines and propioselenetines failed. H. G. M.

Inhibition of photochemical reactions by nitric oxide.—See A., I, 370.

Kinetics of polymeric aldehydes. IV. Mechanism of the process of dissolution of polyoxymethylenes. J. LÖBERING (Ber., 1937, 70, [B], 967—970).—Determination of the rate of dissolution of polyoxymethylene Me₂ ethers shows that the long chains are dissolved and then become degraded in the solution; with polyoxymethylenes a similar process is very probable. H. W.

β -Heptyl- and β -nonyl-acraldehydes. R. DEL-
ABY (Bull. Soc. chim., 1936, [v], 3, 2375—2382).—
Acraldehyde (I) with $n\text{-C}_7\text{H}_{15}\cdot\text{MgBr}\cdot\text{Et}_2\text{O}$ gives
vinyl- n -heptylcarbinol, b.p. 99—101°/11.5 mm., 114—
116.5°/25 mm. (acetate, b.p. 122—123°/24 mm.), con-
verted by $\text{PBr}_3\text{-C}_5\text{H}_5\text{N}$ into α -bromo- Δ^8 -decene, b.p.
118—121°/17.5 mm. (corresponding α -acetoxyl- (II),
b.p. 132—134°/18 mm., and α -isobutoxy-, b.p. 147—
148°/18 mm., compounds), which with $(\text{CH}_2)_6\text{N}_4$ in
 CHCl_3 yields a quaternary ammonium salt (III),
 $\text{C}_7\text{H}_{15}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{N}:(\text{N}_3\text{C}_6\text{H}_{12})\text{Br}$. Hydrolysis of
(II) with NaOH gives Δ^8 -decenol, b.p. 117—118°/11
mm., oxidised by $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ to Δ^8 -decenal, b.p.
106—108°/12 mm. (semicarbazone, m.p. 168.5°), also
obtained by hydrolysis of (III). Similarly, vinyl- n -
nonylcarbinol, b.p. 131.5—132°/13.5 mm., prepared
from $n\text{-C}_9\text{H}_{19}\cdot\text{MgBr}\cdot\text{Et}_2\text{O}$ and (I), is converted into α -
bromo- Δ^8 -dodecene, b.p. 142—144°/12.5 mm.; this with
 $(\text{CH}_2)_6\text{N}_4$ in CHCl_3 gives a quaternary NH_4 compound,
hydrolysed to Δ^8 -dodecenal, b.p. 108—109°/1 mm.
(semicarbazone, m.p. 165.5—166°; cf. A., 1932, 721).

H. G. M.

Preparation of alkoxyaldehydes by oxidation
of glyceryl α -ethers with periodic acid. L.
PALFRAY and S. SABETAY (Bull. Soc. chim., 1937, [v],
4, 950—951).—Agitation of a mixture of glyceryl
 α - CH_2Ph ether, KIO_4 , H_2SO_4 , and H_2O emulsified by
 $\text{CH}_3\cdot(\text{CH}_2)_{11}\cdot\text{O}\cdot\text{SO}_3\text{Na}$ at room temp. gives CH_2O and
benzyloxyacetaldehyde, b.p. 115°/15 mm. (semi-
carbazone, m.p. 120°).

H. W.

Acid character of monoximes. A. GANDINI
and (SIGNA.) C. STRANEO (Gazzetta, 1937, 67, 104—
113).— p_H of aq. solutions of various aliphatic and
aromatic aldoximes and ketoximes, and of alicyclic
ketoximes, is determined potentiometrically. Alkaline
 p_H of monoximes is due to impurities (NH_2OH , NH_3);
the highly purified oximes are slightly acid, in accord-
ance with the normal formulæ. Absorption spectra
are also determined.

E. W. W.

**Study of the α - and β -aldoses and their solu-
tions by bromine oxidation and mutarotation
measurements.** H. S. ISBELL and W. W. PIGMAN
(J. Org. Chem., 1937, 1, 505—539).—When α - and
 β -pairs of sugars have the O-ring on the right in the
projection formulæ, the more dextrorotatory member
is termed α ; when the O-ring is on the left, the less
lævorotatory member is termed β . All aldoses thus
termed β are oxidised by Br more rapidly than are the
 α -isomerides. The O-ring of pentoses is not in the
plane of the C atoms and the mol. as a whole is asym-
metric; the configuration of the ring in pentoses is
allotted by comparison with hexoses. Assignment of
structures on the above system is discussed in detail.
The rate of oxidation of equilibrium solutions of
sugars is at first that of the β - and later that of the
 α -form; the amounts of α - and β -forms present in the
mixture, calc. from the rates of oxidation, are com-
pared with the amounts calc. from $[\alpha]$ on the assump-
tion that only α - and β -forms are present. The
approx. correspondence of the two methods shows
that the equilibrium mixture contains mainly α - and
 β -forms, but possibly also other forms, particularly
for galactose (I), arabinose (II), talose (III), and ribose
(IV); part of the equilibrium mixture of (IV), how-

N* (A., II.)

ever, is oxidised more rapidly than the β -form, which
may thus be incorrectly designated. The rate of
oxidation of the equilibrium mixture from
(d -gulose) $_2$, $\text{CaCl}_2\cdot\text{H}_2\text{O}$ (V) indicates existence of 32%
of the unknown β -form. At 0° and 20° mutarot-
ation of α - and β - d -glucose and -mannose, α - d -
gulose, $\text{CaCl}_2\cdot\text{H}_2\text{O}$ (V), α - and β - d -lyxose, α - l -rhamnose,
 α - and β -lactose, and β -maltose is a first-order
reaction, that of α - and β - d -(I), α - and β - l -(II), β - l -
(II), $\text{CaCl}_2\cdot 4\text{H}_2\text{O}$, d -mannose, $\text{CaCl}_2\cdot\text{H}_2\text{O}$, α - d -(III), and
 l -(IV) is complex. Temp. coeffs. are determined for
the mutarotation of 20 sugars; α - and β -forms muta-
rotate 8.34 and 5.32 times, respectively, faster at 20°
than at 0°. Mutarotations occurring when equi-
librium mixtures of (I), (II), and (III) are cooled give
maxima, showing that constituents other than the
 α - and β -forms are present. $[\alpha]$ of a freshly prepared
solution of α - and β - d -(I) in proportions corresponding
with the equilibrium $[\alpha]$ decreases to a min. and then
returns to the original val., which proves conclusively
the presence of other modifications. The following
approx. contents of α -form in the equilibrium mixtures
are calc.: d -glucose 37, d -mannose 69, d -(I) 31,
 d -(III) 56, (V) 18.5, l -(II) 32.4 (26.5), d -xylose 32,
 d -lyxose 80, d - and l -ribose 89, l -rhamnose 69, lactose
37, maltose 37.

R. S. C.

Oxidation of carbohydrates in acid solution.
M. R. EVERETT and F. SHEPPARD (Univ. Oklahoma
Med. School, Dept. Biochem., 1937, 66 pp.).—Results
are recorded of a study of the oxidation of many carbo-
hydrates by $\text{Br}\text{-H}_2\text{O}$ in acid solution, identification of
the products being based on the Sumner/Folin-Wu
ratios of glucose equivs., mol. optical rotations, and
ratios and mols. of acid/reducing material. The stages
of oxidation of aldoses are (1) formation of mono-
carboxylic lactones, (2) production of dicarboxylic and
keturonic acids (I), and (3) oxidation of (I). Ketoses
are partly changed to l -keturonic acids (II). Sugar
alcohols and non-reducing glucosides are first con-
verted into ketoses and then partly oxidised to (II).
Bromide retards all stages of oxidation, particularly
(2), hence more (I) is formed in dil. solutions of sugar.
Buffers accelerate all stages and cause production of
mixtures of (I). Increased temp. does not invariably
cause the same acceleration of the several reactions.
With ketoses, α -glucosides (III), methylpentoses (IV),
and d -glucosamine, oxidation is not distorted; with
other aldoses, reducing disaccharides, and β -glucosides
(V), a greater formation of non-reducing acids occurs.
Oxidation paths are determined by substitution at
 $\text{C}_{(1)}$, *cis-trans*-isomerism of the intermediate C atoms,
and substitution at $\text{C}_{(6)}$. The first is manifested in the
great differences between α - and β -glucosides, the
second determines the relationship of isomeric sugars,
whilst the third becomes important for (IV) and
dicarboxylic acids. A biological significance of *cis-trans*-
isomerism is indicated. Oxidation of glucosides
provides a chemical method for distinguishing be-
tween α - and β -isomerides in solution. With hexo-
sides, colour tests suffice to detect this difference but
optical activity is applicable to all glucosides. Only
reducing (III) capable of forming bionic lactones
exhibit appreciable changes of rotation during oxida-
tion; these are \ll the marked changes of (V). (III)

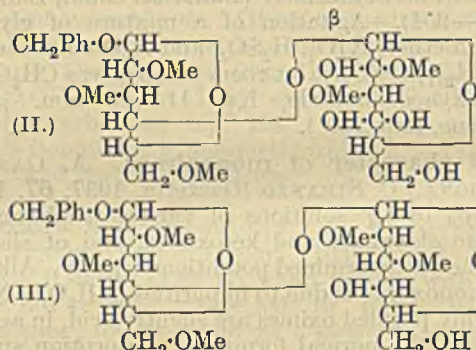
and (V) differ in rates of hydrolysis and oxidation mechanisms. (V) follow the rapid oxidation paths of their component units; the *sec.*-OH of (III) are more slowly oxidised without hydrolysis. At higher temp. these reactions become more nearly identical for the two series. The effects of $\alpha\beta$ -isomerism extend to linkings in anhydro-sugars and polysaccharides. Complications appear in the former when both ordinary ring structures and glucosidic O bridges are present so that some resemble (III) and others (V). *cis-trans*-Isomerism of cyclic C atoms exerts its influence on oxidation *via* ring stability and lactone equilibria. Content of (I) and mol. optical rotations of oxidised sugar solutions are predictable from this isomerism. Optimal conditions for the formation of (I) are provided by perfectly compensated types of cyclic *trans* isomerism; minimal conditions by complete *cis* arrangement. (I) are formed from pentoses through furanose and γ -lactone modifications, from hexoses through pyranose and δ -lactone, and from heptoses through ϵ -oxide form and ϵ -lactone. In many respects the oxidation of carbohydrates by HNO_3 resembles that by Br but the latter is advantageous for analytical studies. Unoxidised anhydro-sugars of the α -D-glucosan series show the same remarkable behaviour with analytical reagents as do their reducing polymericides. H. W.

Dibenzylidene-glucose and -glycuronic acid from 6-benzoyldiethylmercaptoglucose. Synthesis of another dibenzylideneglucose from 4:6-benzylideneglucose. P. E. PAPADIKIS (J. Amer. Chem. Soc., 1937, 59, 841—843).—Diethylmercaptoglucose 6-benzoate (modified prep.), m.p. 114°, $[\alpha]_D^{25} +47.23^\circ$ in CHCl_3 , with ZnCl_2 in PhCHO gives (1:2:3:5)-dibenzylideneglucose 6-benzoate, m.p. 156°, stable to Fehling's solution, hydrolysed by hot KOH-EtOH or cold NaOMe-CHCl_3 to (1:2:3:5)-dibenzylideneglucose (I), m.p. 163°, which with NaOBr in aq. $\text{C}_6\text{H}_5\text{N}$ gives a little dibenzylideneglycuronic acid, m.p. 175°. Dry 4:6-benzylideneglucose and P_2O_5 in PhCHO give a non-reducing dibenzylideneglucose, m.p. 163°, different from (I). R. S. C.

Glucose 2:3:6-tri-p-toluenesulphonate. K. HESS and L. KINZE (Ber., 1937, 70, [B], 1139—1142).—1- α -Bromoglucose 4-acetate 2:3:6-tri-p-toluenesulphonate (I), obtained by fission of starch p-toluenesulphonate by HBr-AcOH , is smoothly converted by a large excess of AgOAc in warm AcOH into β -glucose 1:4-diacetate 2:3:6-tri-p-toluenesulphonate, two forms, m.p. 140—142° and 150—151°, respectively, $[\alpha]_D^{20} +17.6^\circ$ in CHCl_3 , $+39.3^\circ$ in C_6H_6 , $+19^\circ$ in COMe_2 . Glucose 4-acetate 2:3:6-tri-p-toluenesulphonate (II), $[\alpha]_D^{20} +24.6^\circ$ in CHCl_3 , $+60.0^\circ$ in C_6H_6 , $+27.8^\circ$ in COMe_2 , obtained from (I), H_2O , and a large excess of Ag_2O , is a mixture of the α - and β -forms which could not be isolated individually; addition of AgNO_3 , application of Schlubach's method, or use of dry TiOH did not give improved results. Treatment of (II) with Ac_2O containing KOAc or NaOAc gives a mixture of glucose 1:4-diacetate 2:3:6-tri-p-toluenesulphonates (III), m.p. 86—93° (indef.), $[\alpha]_D^{20} +65.2^\circ$ in C_6H_6 , $+48.9^\circ$ in CHCl_3 , which could not be separated into individuals. (I) is readily transformed by HgCl_2 in boiling C_6H_6 into 1- α -chloroglucose 4-

acetate 2:3:6-tri-p-toluenesulphonate, m.p. 173—174°, $[\alpha]_D^{20} +80.7^\circ$ in CHCl_3 , $+70.3^\circ$ in COMe_2 , $+132.2^\circ$ in C_6H_6 [also derived from (II) and p-C₆H₄Me·SO₂Cl in $\text{C}_5\text{H}_5\text{N}$ at room temp.], which does not react with mol. Ag, Na powder, or Ag_2O . Treatment of (III) with NaI in COMe_2 at 90° and then at 115° leads to 6-iodo- β -glucose 1:4-diacetate 2:3-di-p-toluenesulphonate, m.p. 189—190° (decomp.), $[\alpha]_D^{20} +13.0^\circ$ in CHCl_3 , $+22.1^\circ$ in C_6H_6 , $+10.1^\circ$ in COMe_2 . H. W.

Partly methylated disaccharides. I. K. HESS, H. VON HAMMERSTEIN, and W. GRAMBERG (Ber., 1937, 70, [B], 1134—1138).—Benzylcellobioside is shaken with ZnCl_2 and PhCHO and the product is poured into light petroleum; the powdery residue is treated with $\text{C}_5\text{H}_5\text{N}$ (to remove ZnCl_2) and, after removal of the solvent, with abs. EtOH , thus giving benzylidene- β -benzylcellobioside (I), $[\alpha]_D^{20} -47.0^\circ$ in MeOH , -47.8° in $\text{C}_5\text{H}_5\text{N}$. Removal of CHPh from (I) can be effected with 0.001N- H_2SO_4 at 100° or by 0.01N- HCl-MeOH . (I) in small quantities with Ag_2O and MeI affords benzylidenepentamethyl- β -benzylcellobioside, m.p. 140°, $[\alpha]_D^{20} -53.2^\circ$ in CHCl_3 , -48.0° in MeOH , -45.8° in COMe_2 , hydrolysed to 2:3:6:8:10-pentamethyl- β -benzylcellobioside (II), m.p. 140°, $[\alpha]_D^{20}$



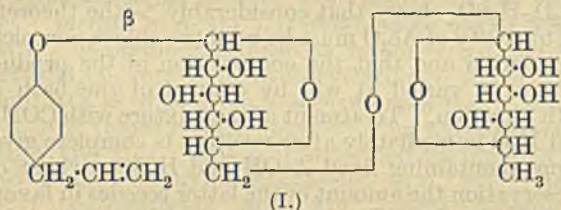
-42.2° in CHCl_3 , -42.5° in MeOH . Treatment of acetobromomaltose with $\text{CH}_2\text{Ph}\cdot\text{OH}$ and Ag_2CO_3 and hydrolysis of the product with $\text{NH}_3\text{-MeOH}$ at 0° yields β -benzylmaltose, transformed by PhCHO and ZnCl_2 into benzylidene- β -benzylmaltoside, m.p. (indef.) 110—116°, $[\alpha]_D^{20} +27.3^\circ$ in MeOH , $+21.0^\circ$ in CHCl_3 , $+31.0^\circ$ in COMe_2 . This is methylated to benzylidenepentamethyl- β -benzylmaltoside, m.p. 132—133°, $[\alpha]_D^{20} +33.0^\circ$ in MeOH , $+29.6^\circ$ in COMe_2 , $+38.4^\circ$ in CHCl_3 , hydrolysed to 2:3:6:8:10-pentamethyl- β -benzylmaltoside (III), m.p. 103—104°. H. W.

Anthranol- β -D-glucoside. J. H. GARDNER and T. F. McDONNELL (J. Amer. Chem. Soc., 1937, 59, 857—858).—Anthrone, acetobromoglucose, and KOH in aq. COMe_2 give anthranol- β -D-glucoside tetra-acetate, m.p. 205—205.2°, converted by Ba(OH)_2 in aq. EtOH at 60° into the free glucoside, $+ \text{H}_2\text{O}$, m.p. 204—206°, which is hydrolysed by 0.05N- HCl (1 hr.; to anthrone) or -KOH (30 min.; to anthrone and dianthrone) and by 9% aq. borax (64% in 1 hr.). Barbaloin is thus not an anthranol glucoside. R. S. C.

Glucoside of Belamcanda chinensis (L.) Leman (Pardanthus chinensis, Ker.), shekanin (tectoridin). C. MANNICH, P. SCHUMANN, and W. H. LIN (Arch. Pharm., 1937, 275, 317—328).—Shekanin

(I), m.p. 257° (decomp.), $[\alpha]_D^{20} -29.4^\circ$ (Ac_6 derivative, m.p. 182°, $[\alpha]_D^{20} -34.9^\circ$ in C_6H_6), isolated in 1.5% yield from the rhizome of this plant by EtOH, is proved to be identical with tectoridin (isolated from *Iris tectorum* with $[\alpha]_D^{20} -29.95^\circ$) by hydrolysis to glucose and tectorigenin (II), m.p. 230° (decomp.) (Ac_3 , m.p. 190°, and Bz_3 derivative, m.p. 230°; *Me*₂ ether, m.p. 188°, and its *Ac* derivative, m.p. 213—214°). The *Me* ether, m.p. 230°, of (I) with 38% HCl gives the 4'-*Me* ether (III), m.p. 191—192°, of (II). With HBr-AcOH (II) gives 5 : 6 : 7 : 4'-tetrahydroxyisoflavone, m.p. about 270° (Ac_4 derivative, m.p. 217—220° after sintering), with 65% HNO_3 gives picric acid, and with KOH gives iretol, *p*-OH·C₆H₄·CH₂·CO₂H, and HCO₂H. KOH converts (III) into iretol and *p*-OMe·C₆H₄·CH₂·CO₂H. R. S. C.

Synthesis of lusitanicoside (chavicol- β -rutinoside), the glucoside from *Cerasus lusitanica*, Lois. G. ZEMPLÉN and A. GERECs (Ber., 1937, 70, [B], 1098—1101).—Rutinoside hepta-acetate (β -1-*l*-rhamnosido-6-*d*-glucose β -hepta-acetate) in CHCl_3 is converted by HBr in AcOH at 0° into α -acetobromorutinoside [α -acetobromo- β -1-*l*-rhamnosido-6-*d*-glucose], m.p. 130.5—131°, $[\alpha]_D^{18} +90.68^\circ$ in CHCl_3 , which is converted by chavicol and KOH in COMe_2 -H₂O into chavicolrutinoside hexa-acetate, m.p. 171.5°, $[\alpha]_D^{18} -48.43^\circ$ in CHCl_3 . This is hydrolysed by NaOMe



in abs. MeOH to chavicol- β -rutinoside, m.p. 188.5°, $[\alpha]_D^{18} -73.86^\circ$ in H₂O, identical with the lusitanicoside of Héressey *et al.* (A., 1932, 662), which is therefore (I).

H. W.

Ring structure of xylal. W. N. HAWORTH, E. L. HIRST, and C. S. WOOLVIN (J.C.S., 1937, 780—782).—Xylal diacetate deacetylated and methylated (Me_2SO_4 and NaOH followed by MeI and Ag_2O) affords dimethylxylal (I), b.p. 73°/17 mm., $[\alpha]_D^{18} -180^\circ$ in CHCl_3 . (I), oxidised in H₂O by BzO_2H in Et₂O, followed by methylation (NaOH - Me_2SO_4 and MeI- Ag_2O) and hydrolysis (HCl), affords trimethyl-lyxose and -xylose, proving the pyranose structure of xylal.

J. D. R.

Polysaccharides. XXIV. Yeastmannan. W. N. HAWORTH, E. L. HIRST, and F. A. ISHERWOOD (J.C.S., 784—791).—Extraction of yeast with aq. NaOH, followed by formation of a $\text{Cu}(\text{OH})_2$ complex, decomp. of this by HCl, and repeated pptn. by EtOH from H₂O yields yeast mannan, (I), ($\text{C}_6\text{H}_{10}\text{O}_5$)_n, $[\alpha]_D^{18} +89^\circ$ in H₂O {acetate (II), by Ac_2O - $\text{C}_5\text{H}_5\text{N}$, $[\alpha]_D^{18} +62^\circ$ in CHCl_3 }. Methylated mannan, $[\alpha]_D^{18} +85^\circ$ in CHCl_3 [from (I) or (II) by Me_2SO_4 -NaOH], is hydrolysed by 1% HCl in MeOH at 150° to tetramethylmethylmannopyranoside (III), b.p. 120—125°/0.07 mm., 2 : 3 : 4-trimethylmethylmannoside (IV), b.p. 145—155°/0.1 mm., and 3 : 4-dimethylmethylmannoside (V), b.p. 138—145°/0.04 mm., the proofs of these structures being as follows. (III) is hydrolysed (H_2SO_4) to tetra-

methylmannose, recognised as the anilide and mannonolactone. (IV) is hydrolysed (H_2SO_4), at a rate indicating a pyranoside structure, to 2 : 3 : 4-trimethylmannose (VI), which is oxidised (Br -H₂O) to 2 : 3 : 4-trimethylmannonolactone, b.p. 135°/0.02 mm., m.p. 91—92°, $[\alpha]_D^{20} +138^\circ$ in H₂O. (VI) is oxidised (HNO_3) to 2 : 3 : 4-trimethylmannosaccharic acid (diamide, m.p. 191°). (V) is hydrolysed (H_2SO_4 ; rate indicates a manno-pyranoside structure) to 3 : 4-dimethylmannose monohydrate, (VII), m.p. 107—109°, $[\alpha]_D^{20} +3^\circ$ in H₂O, oxidised (Br -H₂O) to 3 : 4-dimethylmannonolactone, m.p. 157—158°, $[\alpha]_D^{20} +174^\circ$ in H₂O, the rate of hydrolysis of which indicates a δ -structure, converted by NH_3 -MeOH into 3 : 4-dimethylmannonamide, m.p. 140°, $[\alpha]_D^{20} +22^\circ$ in H₂O, which with NaOCl yields NaCNO, indicating a free OH at C₍₂₎. (VII) yields an osazone with no loss of OMe, and with MeOH-HCl the $[\alpha]$ is unaltered, showing substitution at C₍₄₎. The structural unit of yeast mannan consists, therefore, of three mannose residues; one is attached by its reducing group to another, and thus forms a terminated side-chain, one is attached at C₍₁₎ and C₍₆₎ to the other two, and the third is attached to other residues at C₍₁₎, C₍₂₎, and C₍₆₎. J. D. R.

Polysaccharides. XXV. α -Amylodextrin. W. N. HAWORTH, E. L. HIRST, H. KITCHEN, and S. PEAT (J.C.S., 1937, 791—795; cf. A., 1935, 1355).—Starch, with β -amylase from wheat, at 38° affords maltose and α -amylodextrin (I), $[\alpha]_D^{18} +167^\circ$ in H₂O, which yields an acetate (II) with Ac_2O - $\text{C}_5\text{H}_5\text{N}$ or with Ac_2O - AcOH - Cl_2 - SO_2 . Three specimens of methylated amylo-dextrin, from (I) by NaOH - Me_2SO_4 and from two specimens of (II) by deacetylation and methylation, yield, by the end-group method of assay, 9.8, 10.5, and 10.4%, respectively, of tetramethylglucose, indicating a chain length of 11—12 glucose units. It is considered that this represents genuine α -amylo-dextrin, which is not identical with that formerly described (*loc. cit.*), where a length of 16—17 units was found. J. D. R.

Mol. wt. of limit-dextrin. K. MYRBÄCK (Svensk Kem. Tidskr., 1937, 49, 145—152).—The diffusion of limit-dextrin in NaCl aq. gives vals. for *M* from 2240 to 3300, in agreement with those calc. from the reducing power. The material is homogeneous and does not show any ageing effects.

M. H. M. A.

Degradation of methylated inulin to hexamethyldifructosan. W. N. HAWORTH, E. L. HIRST, and F. A. ISHERWOOD (J.C.S., 1937, 782—784).—Drastic methylation of deacetylated inulin acetate or dimethylinulin leads to methylated inulin with strongly negative $[\alpha]$. Fully methylated inulin, $[\alpha]_D^{20} -55^\circ$ in CHCl_3 , after boiling for 50 hr. with MeI- Ag_2O -MeOH is unchanged, but the presence of HI in the MeI affords hexamethyldifructosan, b.p. 180°/0.1 mm., $[\alpha]_D^{20} +59.3^\circ$, hydrolysed (H_2SO_4) to 3 : 4 : 6-trimethylfructofuranose. The strong positive $[\alpha]$ of the methylated inulin of Irvine and Steele (cf. J.C.S., 1930, 117, 1474) is, therefore, due to depolymerisation. J. D. R.

White oak cellulose. C. D. BIRD and G. J. RITTER (J. Amer. Chem. Soc., 1937, 59, 802—803).—White oak holocellulose (I) resembles that from maple

and spruce, contains OMe 1.64, Ac 3.07, and pentosans 23.4%, and yields 1.56% of CO₂. Extracted white oak wood contains lignin (OMe 22.44%) 23.4, OMe 6.44, Ac 2.37, and pentosans 18.7%, and yields 1.2% of CO₂.
R. S. C.

Decomposition of ethers and esters of cellulose with sodium in liquid ammonia. P. SCHORIGIN and N. N. MAKAROVA-SEMLJANSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 509—511).—Benzyl-cellulose with Na in liquid NH₃ yields cellulose and (CH₂Ph)₂. The reaction product of trimethylcellulose and Na in liquid NH₃, treated with CO₂, gives a small yield of an acidic cellulose, indicating that a Na-cellulose with a C-Na structure is formed. Under similar conditions, cellulose acetate is completely deacetylated.
J. D. R.

Nitration of cellulose. A. BOUCHONNET, F. TROMBE, and G. PETITPAS (Bull. Soc. chim., 1937, [v], 4, 894—904).—HNO₃-H₂O with <33% H₂O yields stable cellulose nitrates but causes hardening and considerable diminution in the final val. of the product. These drawbacks can be overcome by use of HNO₃ containing alkali nitrates, sulphates, or phosphates, whereby products of high N content are obtained. Similar results are attained by the action of conc. HNO₃ on cellulose nitrates of lower N content obtained by means of HNO₃-H₂SO₄ or HNO₃-salts.
H. W.

Highly polymerised compounds. CLIV. Cellulose acetates and celluloses. H. STAUDINGER and G. DAUMILLER (Annalen, 1937, 529, 219—265).—The highly polymerised nature of the insol. cellulose triacetates (I) obtained by the action of Ac₂O-C₅H₅N on cotton or ramie is established by their hydrolysis to celluloses (II) of the same high mol. wt. as the initial materials. Only strongly degraded (II) of degree of polymerisation <500 yield sol. acetates. Attempts to obtain more freely sol. esters by causing irregularity in structure by use of a mixture of acylating reagents did not lead to the desired result. Treatment of (I), re-pptd. from Schweitzer's reagent, with C₅H₅N until all the H₂O is displaced and then with C₅H₅N-Ac₂O gives eucolloidal (II), sol. in C₂H₂Cl₄ or *m*-cresol and with more difficulty in CHCl₃, freely sol. in HCO₂H, in which they suffer degradation. They do not age. A continuous series of polymeric-homologous triacetates similar to the trinitrates is thus available. Investigation of the viscosity of (I) in CHCl₃ and *m*-cresol shows that the polymeric homologues of very varied method of prep. have the same *K_m* const. Also, from the simplest to the most complex (I) the same relationship maintains between mol. wt. and sp. viscosity of equally conc. dil. solutions. All the acetates therefore have the same structure and the same form and are thus polymeric-homologous products. From the osmotically determined mol. wts. and the η_{sp}/c vals. the *K_m* const. for cellite are calc. in COMe₂ and *m*-cresol; they are > those of (I) in *m*-cresol. Revision of the *K_m* const. for (II) indicates the necessity of doubling the mol. wt. hitherto adopted; its degree of polymerisation is ≈ 2000 , in harmony with investigation of the mol. wt. of cellulose nitrate. The *K_m* const. for (II) and its derivatives do not differ very greatly from one another but are widely different

from those of starch and its derivatives. The viscosity relationships of (II) show that eu-, meso-, and hemi-colloidal products have the same structure and that in all of them the glucose residues are united straight, unbranched chains. The *K_m* const. are very close to those calc. for products of extended thread form which contain rings in the chain. The conversion of (II) into polymeric-analogous products establishes the macromol. structure of the most complex members by the classical methods of org. chemistry.
H. W.

Reversibility of the viscosity of solutions of cellite in acetic acid. K. HESS and W. PHILIPPOFF (Ber., 1937, 70, [B], 1143—1148).—1% solutions of cellite in AcOH are diluted to 0.05% and again conc. to 1%, whereby the sp. viscosity of the original solution is again attained. The reversibility indicates that the apparent rupture of cellulose acetates observed osmotically by Hess and Ulmann is not attributable to fission of the bridges by a type of hydrolysis.
H. W.

Preparation of cellulose acetates. L. CLÉMENT and C. RIVIÈRE (Bull. Soc. chim., 1937, [v], 4, 869—880).—Bleached cotton linters is immersed in a mixture of AcOH and H₂SO₄ at 18—20°, whereby hydro-cellulose is produced and there appears to be a temporary fixation of H₂SO₄ probably as an additive compound. Treatment of the product with AcOH-Ac₂O-H₂SO₄ shows that considerably > the theoretical quantity of Ac₂O must be used to achieve complete acetylation and that the composition of the product cannot be varied at will by control of the bath as with nitration. Treatment of the mixture with COMe₂ and H₂O immediately after reaction is complete gives a ppt. containing fixed AcOH and H₂SO₄, whilst on preservation the amount of the latter recedes in favour of the former. The primary acetates containing much OAc appear to be mixtures of cryst. and amorphous phases, the former of which disappears during progressive hydrolysis, and when the solubility of the product in COMe₂ is complete, the X-ray diagram is ill-defined and without rings. Further hydrolysis leads to cryst. cellulose. Halogen acids are much more effective catalysts of hydrolysis than are H₂SO₄ or HClO₄, which are of about equal merit. Generally, good accelerators of hydrolysis are poor catalysts of acetylation. The quantity of H₂O used has a profound influence on the products of hydrolysis. With < the theoretical quantity hydrolysis is observed, but the proportion of residual SO₃ is considerable. With about the theoretical amount, hydrolysis of SO₄ becomes pronounced whilst that of OAc remains regular and without considerable variations. With double the quantity a great variation is not observed with respect to OAc whilst the amount of SO₄ remains const., whereas a larger proportion of H₂O causes further removal of AcOH accompanied, apparently, by a fresh fixation of H₂SO₄.
H. W.

Effect of pressure on the reactions between amines and alkyl halides in acetone.—See A., I, 366.

Action of liquid ammonia on organic halogeno-compounds. J. VON BRAUN [with R. LUTE, K. C. WARNE, W. PINKERNELLE, W. ROHLAND, A. POHL, F. DENGEL, and H. ARNOLD] (Ber., 1937, 70,

[B], 979—993).—The yield of primary amine from org. halogeno-compounds is greater when liquid NH_3 is used than with $\text{NH}_3\text{-H}_2\text{O}$ or $\text{NH}_3\text{-EtOH}$ and increases very greatly with increasing mol. wt. of halide independently of constitutional details. The method is very advantageous for the prep. of ether-bases, *sec.* primary and *tert.*-primary diamines, monoacylated diamines, decarboxypeptides, and quinoline derivatives with $2\text{-CH}_2\text{Cl}$ whereby nuclear Cl is little affected. With compounds $\text{Cl}[\text{CH}_2]_n\text{Cl}$ spiran formation is observed when the val. of n is suitable; otherwise diamines are mainly produced. With very reactive halogen the formation of imino- rather than amino-compounds is observed.

$\text{C}_6\text{H}_{11}\text{Br}$ and liquid NH_3 at room temp. afford $\text{C}_6\text{H}_{11}\text{NH}_2$ (about 10%) and about 80% of $\text{NH}(\text{C}_6\text{H}_{11})_2$, possibly containing $\text{N}(\text{C}_6\text{H}_{11})_3$. $\text{C}_8\text{H}_{17}\text{Br}$ gives $\text{C}_8\text{H}_{17}\text{NH}_2$ (45%) and $\text{NH}(\text{C}_8\text{H}_{17})_2$ (43%), whilst $\text{C}_{12}\text{H}_{25}\text{Br}$ yields almost 90% of $\text{C}_{12}\text{H}_{25}\text{NH}_2$. CH_2PhCl and liquid NH_3 give CH_2PhNH_2 (53%) and $\text{NH}(\text{CH}_2\text{Ph})_2$ (39%), whereas with $\text{NH}_3\text{-EtOH}$ the yields of CH_2PhNH_2 , $\text{NH}(\text{CH}_2\text{Ph})_2$, and $\text{N}(\text{CH}_2\text{Ph})_3$ are respectively 9%, 35%, and 48%. $1\text{-C}_{10}\text{H}_7\text{CH}_2\text{Cl}$ gives $\alpha\text{-C}_{10}\text{H}_7\text{CH}_2\text{NH}_2$ and *di- α -naphthylamine*, b.p. 230—235°/0.3 mm., m.p. 55° (*hydrochloride*, m.p. 230°; *picrate*, m.p. 206°; *NO*-derivative, m.p. 132°). *Tri- α -naphthylamine*, m.p. 178° (*hydrochloride*, m.p. 199°; *picrate*, m.p. 211°), is obtained by use of $\text{NH}_3\text{-EtOH}$. 9-Bromophenanthrene is converted by Mg and $(\text{CH}_3\text{O})_3$ into 9-phenanthrylcarbinol, which with conc. HCl at 100° gives 9-phenanthrylmethyl chloride, m.p. 102° (more readily obtained from phenanthrene, CH_2O , and HCl); this is transformed by liquid NH_3 into 9-aminomethylphenanthrene, m.p. 107° (yield 70%) [*hydrochloride*, m.p. 277° (slight decomp.); *picrate*, m.p. 236°], and *di-9-phenanthrylmethylamine*, m.p. 193° (*hydrochloride*, m.p. 239°; *NO*-compound, m.p. 268°). With $\text{NH}_3\text{-EtOH}$ *tri-9-phenanthrylmethylamine*, m.p. 163° (*hydrochloride*, m.p. 229°; *picrate*, m.p. 190° after softening at 170°), is obtained. $\text{OPh}[\text{CH}_2]_2\text{NH}_2$ and $\text{OPh}[\text{CH}_2]_3\text{NH}_2$ are obtained in 65% and 71% yield respectively from $\text{OPh}[\text{CH}_2]_2\text{Br}$ and $\text{OPh}[\text{CH}_2]_3\text{Br}$. NH_2Ph is transformed by a large excess of $\text{C}_2\text{H}_4\text{Br}_2$ at 100° into non-distillable $\text{NHPh}[\text{CH}_2]_2\text{Br}$, which with conc. HCl at 100° affords β -chloroethylaniline, b.p. 91—94°/1 mm. The latter and liquid NH_3 afford $\text{NHPh}[\text{CH}_2]_2\text{NH}_2$ (65%) and *di- β -anilinoethylamine*, b.p. 215—225°/0.1 mm. [*hydrochloride*, m.p. 233°; (*NO*)₃-compound, m.p. 99°]. $\text{NPhMe}[\text{CH}_2]_2\text{Br}$ similarly affords β -methylanilinoethylamine (I), b.p. 100—112°/0.3 mm. (*picrate*, m.p. 174°; *hydrochloride*, m.p. 205°; *Ac* derivative, m.p. 88°), and *di- β -methylanilinoethylamine*, b.p. 200—202°/0.3 mm. (*hydrochloride*, m.p. 204°). The *NO*-derivative, m.p. 140°, of (I) is transformed by successive treatment with NaHSO_3 and HCl into β -methylanilinoethylamine, b.p. 115—117° (*hydrochloride*, m.p. 132°; *picrate*, m.p. 223°). $\text{NPhEt}[\text{CH}_2]_2\text{Br}$ affords β -ethylanilinoethylamine, b.p. 148—150°/20 mm. (*hydrochloride*, m.p. 153°; *picrate*, m.p. 166°; *Ac* derivative, b.p. 180—185°/0.5 mm., m.p. 100°), and *di- β -ethylanilinoethylamine*, b.p. 223—230°/12 mm. (*hydrochloride*, m.p. 203°; *picrate*, m.p. 176°). $\text{NPhMe}[\text{CH}_2]_3\text{Cl}$ yields γ -methylanilino-propylamine, b.p. 112—115°/0.3 mm. (*hydrochloride*,

m.p. 189°; *picrate*, m.p. 152°; *Ac* derivative, b.p. 168—172°/0.2 mm., and its *NO*-derivative, m.p. 114°, and *di- γ -methylanilinopropylamine*, b.p. 220—222°/0.3 mm. [*hygroscopic hydrochloride*; *picrate*, m.p. 166°; *Ac* derivative, b.p. 250—255°/0.3 mm., and its (*NO*)₂-derivative, m.p. 161°]. γ -Methylaminopropylamine, b.p. 138—139° (*hydrochloride*, m.p. 185°; *picrate*, m.p. 227°), and *di- γ -methylaminopropylamine*, b.p. 122°/15 mm., m.p. 22° (*picrate*, m.p. 175°; *hydrochloride*, m.p. 275°), are described. $\text{NHBz}[\text{CH}_2]_4\text{Cl}$ gives benzoylputrescine, b.p. 186°/0.7 mm. (yield about 70%), and *di- δ -benzamidobutylamine*, b.p. 290°/0.3 mm., m.p. 87° (*hydrochloride*, m.p. 230°), and $\text{NHBz}[\text{CH}_2]_5\text{Cl}$ affords benzoylcadaverine, b.p. 202°/0.5 mm., with *di- ϵ -benzamidoamylamine*, m.p. 69° (*hydrochloride*, m.p. 199°).

3 : 4-Dichloro-2-chloromethylquinoline and liquid NH_3 afford 3 : 4-dichloro-2-aminomethylquinoline, m.p. 104—106° (yield 72%) (*hydrochloride*, m.p. 239°; *picrate*, m.p. 185°; *Ac* derivative, m.p. 170°), and *di-3 : 4-dichloro-2-quinolylmethylamine*, decomp. 162—165° (*hydrochloride*, m.p. 218—220°); with $\text{NH}_3\text{-EtOH}$ at 100° only the *sec.* base is obtained. 3-Chloro-4-anilino-2-chloromethylquinoline yields 3-chloro-4-anilino-2-aminomethylquinoline, m.p. 155° [*hydrochloride*, m.p. 214°; *picrate*, m.p. about 170°; *Ac* derivative (+1H₂O), m.p. 189°], and *di-3-chloro-4-anilino-2-quinolylmethylamine*, m.p. 232° (*hydrochloride*, m.p. 225—230°; *NO*-derivative, m.p. 119°). $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ is transformed by contact with PCl_5 and POCl_3 into 3-chloro-4-p-phenetidino-6-ethoxy-2-chloromethylquinoline, m.p. 118—120° (*hydrochloride*, m.p. 231°; *picrate*, m.p. 155°), which yields 3-chloro-4-p-phenetidino-6-ethoxy-2-aminomethylquinoline, m.p. 110—112° (*hydrochloride*, m.p. 185°; *Ac* derivative, m.p. 143°), and *di-3-chloro-4-p-phenetidino-6-ethoxy-2-quinolylmethylamine*, m.p. 214—216° (*hydrochloride*, m.p. 206°; *Ac* compound, m.p. 160—162° after slight softening).

$\text{Cl}[\text{CH}_2]_{11}\text{Cl}$ gives almost exclusively $\text{NH}_2[\text{CH}_2]_{11}\text{NH}_2$. $\text{Br}[\text{CH}_2]_5\text{Br}$ affords mainly dipiperidinium bromide with very small amounts of piperidine and cadaverine. Similarly $\text{Br}[\text{CH}_2]_4\text{Br}$ give chiefly dipyrrolidinium bromide with some pyrrolidine and 1- Δ^7 -butenylpyrrolidine, b.p. 152—154° (*picrate*, m.p. 107°; *hygroscopic methiodide*, m.p. 178°). $\text{Br}[\text{CH}_2]_3\text{Br}$ affords $\text{NH}_2[\text{CH}_2]_3\text{NH}_2$ and *di- γ -aminopropylamine*, b.p. 210—230°. $(\text{CH}_2\text{Cl})_2$ gives $(\text{CH}_2\text{NH}_2)_2$ and $\text{NH}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$; with $(\text{CH}_2\text{Br})_2$ the yield of primary amine is lower and compounds, $\text{NH}_2[\text{CH}_2]_2[\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2]_n\text{NH}_2$, are produced.

Ph_2 , CH_2O , and HCl give only $(\text{CH}_2\text{Cl})_2$ derivatives whereas HBr affords 4 : 4'-dibromomethyldiphenyl, m.p. 170°, in almost 50% yield. This with liquid NH_3 gives 4 : 4'-diaminomethyldiphenyl, m.p. 135° (*picrate*, m.p. 222°; *Ac*₂ derivative, m.p. 272°; *Bz*₂ compound, m.p. 243°).

H. W.

Synthesis of ethylenic amines. R. PAUL and H. COTTIN (Bull. Soc. chim., 1937, [v], 4, 933—937).—Ethylenic amines are best obtained by reduction of the corresponding nitriles with Na and abs. EtOH. Δ^7 -Pentenitrile, b.p. 145°, obtained in 60% yield by passage of NH_3 and $\text{CH}_2\text{CH}[\text{CH}_2]_2\text{CN}$ over SiO_2

at 480–500°, gives α -amino- Δ^8 -pentene, b.p. 105–106°/767 mm. (*hydrate*, b.p. about 93°; *platinichloride*, decomp. 160°; *picrate*, m.p. 115–116°; *H oxalate*, m.p. 129–130°). α -Cyano- α -allyl- Δ^7 -pentenoic acid passes at 110–120° into α -allyl- Δ^7 -pentenenitrile, b.p. 85°/14 mm., 186°/760 mm., reduced to α -amino- β -allyl- Δ^8 -pentene, b.p. 84–85°/20 mm., 168°/764 mm. (*platinichloride*, decomp. 142–143°; *picrate*, m.p. 138–139; *H oxalate*, m.p. 137°). β -Allyl- Δ^8 -pentenyl bromide, b.p. 74–75°/17 mm., obtained with some δ -bromo- β -allylamyl bromide, b.p. 113–114°/13 mm., by gradual addition of $(\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{C}_5\text{H}_5\text{N}$ to PBr_3 , affords β -allyl- Δ^8 -hexenenitrile, b.p. 90–91°/14 mm., whence α -amino- γ -allyl- Δ^6 -hexene, b.p. 86–18°/23 mm. (*picrate*, m.p. 124°).

H. W.

Highly polymerised compounds. CLVI. Polyammonium compounds of high mol. wt. H. STAUDINGER and H. VON BECKER (Ber., 1937, 70, [B], 879–888).—Simple relationships between viscosity and chain length as with homopolar mol. compounds are not observed with proteins, the sp. viscosity of which varies within wide limits with the $[\text{H}^+]$ and electrolytic addenda. Solutions of proteins which obey Einstein's law contain approx. spherical mols.; proteins which give highly viscous solutions of low concn. and with which the viscosity is not \propto concn. have extended mols. Solutions of Na polyacrylate (heteropolar mol. colloid as model for proteins) do not obey the Hagen-Poiseuille law mainly on account of cluster formation of the thread ions. The polyammonium bromides obtained by Gibbs *et al.* (A., 1933, 381) from $\text{NMe}_2\cdot[\text{CH}_2]_3\cdot\text{Br}$ can be separated by dialysis into less and more viscous fractions the sp. viscosity of which diminishes with increasing concn. Cluster formation is impeded by the presence of HBr and in presence of sufficient electrolyte they behave like homopolar mol. colloids. A more perfect model of the proteins is afforded by polyammonium polyacrylate, which resembles a globulin in its insolubility in dil. NaOH or HCl and its ready solubility in 1.5*N*-NaCl containing a trace of H^+ or OH^- . The relative viscosity of its solutions in 1.5*N*-NaCl containing NaOH or HCl (compared with that of a similar solution of NaCl) is independent of $[\text{H}^+]$ or $[\text{OH}^-]$. H. W.

Betaines. IV. Mechanism of racemisation of salts of ethyl propiobetainate. E. BILMANN, K. A. JENSEN, and H. B. JENSEN (Bull. Soc. chim., 1936, [v], 3, 2295–2305; cf. A., 1935, 331).—(–)-, m.p. 130–131°, $[\alpha]_D^{20}$ –19.64° in EtOH, and (+)-*Et propiobetainate iodide*, m.p. 130–131°, $[\alpha]_D^{20}$ +19.78° in EtOH (prep. described), are racemised at the same speed by a mixture of (+)-*NN-diethyl- β -methylbutylamine*, b.p. 150–151°/765 mm., $[\alpha]_D^{20}$ +17.96°, and its *iodide*, which, as in the case of other *tert.*-amines and their salts, has a considerable influence on the velocity. Racemisation by means of the weak base PEt_3 occurs very slowly. (+)-, m.p. 157–157.5°, $[\alpha]_D^{20}$ +19.60° in EtOH, and (–)-*trimethyl- α -phenylethylamine iodide*, m.p. 156.5–157°, $[\alpha]_D^{20}$ –19.60°, prepared by methylation of the appropriate amine, are not racemised by NaOEt-EtOH during 2 months, whilst *Et (+)- α -dimethylamino-propionate*, b.p. 155.5–156.5°/767 mm., $[\alpha]_D^{20}$ +5.58°,

but not *Et d- α -aminopropionate*, is racemised by NaOEt-EtOH , but more slowly than the betainate. These results support the view that racemisation involves the formation of an intermediate enolate ion.

H. G. M.

Reactions of amino- and imino-acids with formaldehyde. M. LEVY and D. E. SILBERMAN (J. Biol. Chem., 1937, 118, 723–734).—Changes of p_{H} (H electrode) during the titration in presence of alkali of *dl*-alanine, *dl*-valine, *l*-aspartic acid, *l*-tryptophan, *dl*-sarcosine, and *l*-hydroxyproline with CH_2O show that NH_2 -acids may react with 1 or 2 mols., NH -acids with only 1. Similar measurements with asparagine and CH_2O , and measurements of the rate of disappearance of $\text{NH}_2\cdot\text{N}$, show that the product of this reaction is a pyrimidine derivative.

A. LI.

Highly polymerised compounds. CLVII. Measurements of the viscosity of amino-acids. H. STAUDINGER and H. VON BECKER (Ber., 1937, 70, [B], 889–900).—The same relationships between sp. viscosity and chain length are not observed with acylated NH_2 -acids and their esters (containing an acyl group of high mol. wt.) as with purely homopolar compounds; the observed viscosity is $>$ that calc. by an increment. This is attributed to the influence of the many $\text{CO}\cdot\text{NH}_2$ linkings. It is not therefore possible to calculate the chain length in a simple manner from measurements of viscosity as with hydrocarbons and esters. By the addition of the requisite acid chloride to $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}\cdot\text{HCl}$ in $\text{CHCl}_3\text{-C}_5\text{H}_5\text{N}$ the lauryl, m.p. 61.5°, *myristyl*, m.p. 70°, *palmityl*, m.p. 77.5°, and *stearyl*, m.p. 82.5°, derivatives of $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ are obtained. Analogously, sarcosine *Et* ester gives *palmityl*, m.p. 33.5°, and *stearyl*, m.p. 35–37°, compounds whilst *lauryl*, m.p. 132°, *myristyl*, m.p. 133°, *palmityl*, m.p. 133.5°, and *stearyl*, m.p. 134°, derivatives are obtained from glycylglycine *Et* ester. $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ or the requisite acid chloride in presence of aq. NaOH afford the lauryl, m.p. 119.5°, *myristyl*, m.p. 122°, *palmityl*, m.p. 123.5°, and *stearyl*, m.p. 124.5°, derivatives. Sarcosine give the *palmityl*, m.p. 61.5°, and *stearyl*, m.p. 67–68°, compounds whilst *palmityl*, m.p. 113°, and *stearyl*, m.p. 113.5°, derivatives are obtained from alanine.

H. W.

Synthesis of *dl*-alanine in improved yield from α -bromopropionic acid and aqueous ammonia. W. C. TOBIE and G. B. AYRES (J. Amer. Chem. Soc., 1937, 59, 950).—Details are given for obtaining a 65–68% yield in this synthesis.

R. S. C.

Colour reactions of sarcosine and alanine with ferric salts. III. J. V. DUBSKÝ and A. LANGER (Coll. Czech. Chem. Comm., 1937, 9, 137–149).—The following complex salts are prepared, usually by evaporation of aq. solutions of the Fe^{III} salt with sarcosine (*S*), *dl*-alanine (*A*), or glycine (*G*): $\text{FeCl}_3\cdot\text{A} + \text{H}_2\text{O}$, m.p. 115°, decomp. 134°; $\text{FeCl}_3\cdot\text{FeCl}_2(\text{OH})\cdot 3\text{A} + 4\text{H}_2\text{O}$, m.p. 70°, decomp. 105°; $\text{FeCl}_3\cdot 2\text{S} + 0.5\text{H}_2\text{O}$, m.p. 65°; $\text{FeBr}_3\cdot\text{FeBr}_2(\text{OH})\cdot 2\text{S} + \text{H}_2\text{O}$, decomp. 135°; $\text{FeBr}_3\cdot\text{FeBr}_2(\text{OH})\cdot 3\text{S}$; $\text{FeBr}_3\cdot\text{FeBr}_2(\text{OH})\cdot 4\text{S} + 2\text{H}_2\text{O}$, decomp. 135°; $\text{FeCl}_3\cdot\text{FeCl}_2(\text{OH})\cdot 2\text{A} + 4\text{H}_2\text{O}$, m.p. 116°, decomp.

123°; $\text{FeCl}_3 \cdot \text{FeCl}_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, decomp. 120°; $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$, decomp. 126°; $\text{FeBr}_3 \cdot \text{FeBr}_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, decomp. 145°; $\text{FeCl}_3 \cdot \text{FeCl}_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, decomp. 120°; $\text{FeCl}_2(\text{OH})_2 \cdot \text{G} + 2\text{H}_2\text{O}$, decomp. 119°; $\text{FeCl}_2(\text{OH})_2 \cdot 2\text{G} + 1.5\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot \text{FeCl}_2(\text{OH})_2 \cdot 2\text{G} + 2\text{H}_2\text{O}$; $\text{FeCl}_2 \cdot \text{FeCl}_2(\text{OH})_2 \cdot 3\text{G} + 4\text{H}_2\text{O}$; $\text{FeCl}_3 \cdot \text{FeCl}_2(\text{OH})_2 \cdot 2\text{G} + 6\text{H}_2\text{O}$, darkens 120°, decomp. 170°; $2\text{FeCl}_3 \cdot 3\text{HCl} \cdot 3\text{G}$, m.p. 95°; $\text{FeCl}_2 \cdot \text{HCl} \cdot \text{G}$, m.p. 96—140°; $2\text{FeCl}_3 \cdot \text{HCl} \cdot \text{G} + 4\text{H}_2\text{O}$. J. W. B.

Dideuterovaline and dideuteroleucine. C. R. KINNEY and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 897—898).— $\text{CMe}_2\text{Br} \cdot \text{CH}(\text{OEt})_2$, b.p. 80°/28 mm., gives isobutenaldehyde Et_2 acetal, b.p. 136—139°, reduced by H_2 - PtO_2 to isobutaldehyde Et_2 acetal, b.p. 135—136°/745 mm., and by D_2 - PtO_2 in EtOAc to $\alpha\beta$ -dideuteroisobutaldehyde Et_2 acetal, b.p. 133—135°/747 mm., which with NH_4Cl - KCN gives $\beta\gamma$ -dideuterovaline, m.p. 273° (decomp.) (1.5—2° < *dl*-valine); this acid contains 25% < the theoretical amount of D, due to loss during enolisation of the aldehyde. Similarly are obtained $\alpha\beta$ -dideuteroisovaleraldehyde Et_2 acetal, b.p. 164—165°/740 mm., isovaleraldehyde Et_2 acetal, b.p. 167—168°/750 mm., and $\beta\gamma$ -dideuteroleucine, m.p. 271° (decomp.) (2° < *dl*-leucine) (93.5% pure; enolisation much less probable). R. S. C.

Photographic chemistry of cystine. A. STEIGMANN (Phot. Ind., 1937, 35, 357—358; cf. A., 1936, 873).—A general method for producing new compounds containing labile S consists in heating together cystine, in H_2O , with $\text{CH}_2\text{Br} \cdot \text{CO}_2\text{H}$ (or other halogenofatty acids), NaOH (or other alkali or aldehydes), with or without CH_2O . Thus two new compounds (or mixed compounds) formed from the above substances, with and without CH_2O , are named "cystiformin" and "cysticin" respectively; in emulsions they desensitise strongly, but show no other notable properties. J. L.

Selenium-substituted amino-acids. III. Inactive selenocystine. A. FREDGA (Svensk Kem. Tidskr., 1937, 49, 139—145; cf. this vol., 235).—Study of the variation with time of the solubility of (+)- (I) and (—)-selenocystine, singly and as equimol. mixture, indicates the production of the *meso*-form in the solution. The hydrochloride and hydrobromide of (I), *r*-selenocystine hydrochloride. (—)-cystine hydrobromide, and *r*-cystine hydrochloride are described.

M. H. M. A.

Acid amides. K. VON AUWERS (Ber., 1937, 70, [B], 964—967).—According to present chemical and physical evidence, acid amides are typical tautomeric compounds which in the liquid condition give mixtures of the $\cdot\text{CO} \cdot \text{NH}_2$ and $\cdot\text{C}(\text{OH}) \cdot \text{NH}$ forms. According to peculiarities of their components, the position of equilibrium can be greatly, under conditions almost completely, displaced in one or other direction. H. W.

Photochemical properties of the keto-imino-ling.—See A., I, 370.

Transposition of the functional group carboxyl in the form of an ester. J. MILIOTIS (Bull. Soc. chim., 1936, [v], 3, 2365—2367).—Transposition of

carboxyl as ester occurs in the Hofmann degradation of *Et* oxamate with $\text{Br} \cdot \text{KOH}$, the products being $\text{OEt} \cdot \text{CO} \cdot \text{NH}_2$, only in small amount owing to evolution of NH_3 towards the end of the reaction, and EtOH .

H. G. M.

Decarboxypeptides and their derivatives. III. J. VON BRAUN, F. DENGEL, and A. JACOB [in part, with A. BAHN] (Ber., 1937, 70, [B], 994—1001; cf. A., 1930, 73).—Examination of a series of decarboxypeptides shows them to be physiologically inactive when containing NH_2 , NHMe , or NHEt but productive of cramp and lowering of temp. when higher alkyl groups are present; the activity appears to attain a max. with groups of medium size. Peptides which are not composed entirely of natural protein components appear physiologically inactive whatever the magnitude of the alkyl group. $\text{CHMeBr} \cdot \text{COBr}$ and pyrrolidine in dry Et_2O give 1- α -bromopropionylpyrrolidine, b.p. 112—114°/0.2 mm., which with the requisite primary amine afford 1- α -ethylaminopropionylpyrrolidine (N-ethylalanyldicarboxyproline), b.p. 90—95°/0.2 mm. (hydrochloride, m.p. 210°; picrate, m.p. 174°), and 1- α -isoamylaminopropionylpyrrolidine, b.p. 130—135°/0.2 mm. (hydrochloride, m.p. 201°; picrate, m.p. 147°). Addition of $\text{NH}_2 \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$ in Et_2O to $\text{CH}_2\text{Cl} \cdot \text{COCl}$ affords $\alpha\gamma$ -dichloroacetamidopropane, m.p. 125°, transformed by liquid NH_3 at room temp. into $\alpha\gamma$ -diaminoacetamidopropane (hydrochloride, m.p. 165°). $\alpha\gamma$ -Diethylaminoacetamidopropane, b.p. 221°/0.5 mm. (hydrochloride, m.p. 158°), and $\alpha\gamma$ -diisoamylaminoacetamidopropane (hydrochloride, m.p. 158°) are described. Di- α -aminopropionamidopropane (very hygroscopic hydrochloride, m.p. 227°) its Et_2 , b.p. 200—204°/0.4 mm., m.p. 45° (hydrochloride, m.p. 120°), and diisoamyl, b.p. 219—221° (0.2 mm. hydrochloride, m.p. 122°), derivatives have been prepared. Putrescine and $\text{CH}_2\text{Cl} \cdot \text{COCl}$ in $\text{Et}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$ give $\alpha\delta$ -dichloroacetamidobutane, m.p. 131°, which gives $\alpha\delta$ -diaminoacetamidobutane, m.p. 108° (very hygroscopic hydrochloride; Et_2 derivative, m.p. 58°, and its hydrochloride, m.p. 198°; diisoamyl compound, b.p. 220°/high vac., m.p. 42—43°, and its hydrochloride, m.p. 248°). Di- α -bromopropionamidobutane, m.p. 175°, gives di- α -ethylaminopropionamidobutane (hydrochloride, m.p. 67°) and the corresponding Pr_2 (hydrochloride, m.p. 80°), Bu^2 , (hydrochloride, m.p. 58°), diisoamyl (hydrochloride, m.p. 56°), and didecyl compounds, b.p. about 270°/high vac., m.p. 75—77°. $\alpha\epsilon$ -Dichloroacetamidopentane, m.p. 121°, gives $\alpha\epsilon$ -diaminoacetamidopentane, m.p. 91° (hydrochloride, m.p. 207°; Et_2 derivative, m.p. 227—229°/0.5 mm., m.p. 39—41°, and its hydrochloride, m.p. 201°; diisoamyl compound, b.p. 250—252°/0.1 mm., and its hydrochloride, m.p. 180°). Di- α -bromopropionamidopentane, m.p. 135°, gives non-cryst. di- α -aminopropionamidopentane (very hygroscopic hydrochloride, m.p. 123° after softening at 105°; Et_2 derivative, b.p. 230°/0.4 mm. and its hydrochloride, m.p. 100°; diisoamyl compound, b.p. 242°/0.3 mm., m.p. 26°, and its very hygroscopic hydrochloride, m.p. 110°). NH_2Et and $\text{CHBrEt} \cdot \text{COBr}$ afford α -bromobutyrethylamide, b.p. 125—128°/16 mm., m.p. 63°, whence α -ethylamino-, b.p. 120—122°/13 mm., m.p. 43° (hydrochloride, m.p. 113°), and α -isoamylamino-, b.p. 147—152°/16 mm. (hydrochloride, m.p. 84°), -butyrethylamide. α -Ethyl-

amino-, b.p. 177—180°/1 mm. (hydrochloride, m.p. 235°), and α -isoamylamino-, b.p. 180—182°/0.3 mm. (hydrochloride, m.p. 153—155°), are derived from α -bromo- γ -phenylbutyrylamide, m.p. 68—69°. α -Bromo- γ -phenylbutyryl chloride, b.p. 122—125°/1 mm., tends to lose HBr when distilled. *p*-Nitrobenz- β -phenylethylamide, m.p. 151°, is reduced (Pd in MeOH) to *p*-aminobenz- β -phenylethylamide, m.p. 151° (hydrochloride, m.p. 265°). Di-*p*-nitrobenzamidobutane, m.p. 260°, affords α , δ -di-*p*-aminobenzamidobutane, m.p. 243° (Ac_2 derivative, 299°). Tyramine and *p*-NO₂-C₆H₄-COCl yield mono-, m.p. 175°, and di-, m.p. 193°, -nitrobenzoyldecarboxytyrosine which are reduced to the corresponding NH₂-, m.p. 214°, and (NH₂)₂-, m.p. 248°, -compounds. H. W.

Carbonyl cyanide. I. R. MALACHOWSKI, L. JURKIEWICZ, and J. WOJTCOWICZ (Ber., 1937, 70, [B], 1012—1016).—CO(CH₂N·OH)₂ is transformed by Ac₂O at 100° into the diacetate, m.p. 80—81° after softening at 75—77°, which passes at 110°/12 mm. into AcOH and acetoximinoacetoneitrile (I), b.p. 110°/9 mm., m.p. (indef.) about 90°. (I) is readily hydrolysed by H₂O to CO₂, HCN, and AcOH. It is transformed by EtOH into *Et* acetoximinoacetate, b.p. 113°/8 mm., also obtained from *Et* oximinoacetate and Ac₂O at 90°. At 160° (I) yields AcOH and carbonyl cyanide, b.p. 65.5° (corr.)/740 mm., m.p. -36° to -35°, which does not tend to polymerise and can be kept unchanged in vessels of resistant glass in absence of moisture. It reacts immediately and explosively with cold H₂O giving HCN and CO₂. With cold EtOH it yields CN·CO₂Et. H. W.

Action of halogen compounds of arsenic and phosphorus on acetylenic carboxylic acids. I. Addition of arsenic chloride to tetrolic acid. V. O. MOCHNATSC and V. S. BAGNIUK (Compt. rend. Acad. Sci., U.R.S.S., 1937, 14, 553—558).—CMe₂C·CO₂H and AsCl₃ at 110—115° afford the normal adduct, AsCl₂·CMe₂·CCl·CO₂H, but at 120—130° decarboxylation occurs to give, after KOH-treatment, α -chloro- β -arsinoxy- Δ^2 -propene. At 140° the product is α -chloro- Δ^2 -propenyl- β -arsine, m.p. 91.5—92°. At 150—155° CMe₂C·CO₂H with AsCl₃ gives AsO·CMe₂·CHCl; at lower temp. mixtures containing mainly the arsinoxy-acid are obtained. J. W. B.

Phosphinetes and arsenetines. E. BILLMANN and K. A. JENSEN (Bull. Soc. chim., 1936, [v], 3, 2306—2309).—CHMeBr·CO₂Et (I) when treated with PET₃, alone or in Et₂O, gives *Et* propiotriethylphosphetinate bromide, CHMe(PET₃)Br·CO₂Et, m.p. 113—114°. Similarly, *d*-CHMeBr·CO₂Et (II) yields a partly active product, instantly racemised by NaOEt-EtOH, rapidly by NEt₃-EtOH, and slowly by EtOH. CHMeBr·CO₂H and PET₃ in an atm. of CO₂ yield propiotriethylphosphetinate hydrobromide, CHMe(PET₃)Br·CO₂H. *Et* propiotrimethylphosphetinate bromide, m.p. 124—125°, and a partly active form, [α]_D²⁰ +10.03° in EtOH, were similarly prepared. (II) with PPr₃ gives only *r*-*Et* propiotripropylphosphetinate bromide. By similar methods (I) with AsEt₃ gives *Et* propiotriethylarsenetinate bromide, CHMe(AsEt₃)Br·CO₂Et, m.p. 69—70°, the same inactive form being also obtained from (II). H. G. M.

Organic derivatives of silicon. F. S. KIPPING (Proc. Roy. Soc., 1937, A, 159, 139—147).—Bakerian lecture. G. D. P.

Electronegative series of organic radicals. A. N. NESMEJANOV and K. A. KOTSCHESCHKOV (Sci. Rep. Moscow State Univ., 1934, No. 3, 283—289).—Two reactions take place between SnX₂ (X = Cl, Br) and HgR₂ in EtOH, viz., HgR₂ + SnX₂ → SnR₂X₂ + Hg, and HgR₂ + SnX₂ + 2EtOH → 2RH + (OEt)₂SnX₂. Domination of the latter over the former increases in proportion to the electronegative character of R, in the series of diminishing electronegativity R = ·CH(CO₂Et)₂, *p*-NH₂·C₆H₄, *p*-OH·C₆H₄, *o*-OMe·C₆H₄, β -C₁₀H₇, *o*-, *p*-C₆H₄Me, *p*-C₆H₄I, *p*-C₆H₄Br, *p*-C₆H₄Cl, *p*-C₆H₄F, Ph, *p*-C₆H₄·CO₂Et, CH₂Ph. This series is practically identical with that of Kharasch (A., 1927, 165). It is concluded that the reactions do not involve ionisation of the substrate. R. T.

Mechanism of formation of mercuri-organic compounds through diazo-compounds. A. N. NESMEJANOV (Sci. Rep. Moscow State Univ., 1934, No. 3, 291—296).—Liberation of Hg is not an intermediate phase of the reaction PhN₂Cl·HgCl + 2Cu → HgPhCl + 2CuCl + N₂, as Cu may be replaced by Ag, which cannot displace Hg. In addition, Cu may be replaced by Cu-bronze, Al, Fe, Zn, Mg, or SnCl₂. CHN₂·CO₂Et and HgCl₂ yield Hg[CCl(HgCl)·CO₂Et]₂, CH₂Cl·CO₂Et, and N₂. R. T.

Oxidation of non-electrolytic cis-bivalent platinum compounds with sulphuric acid.—See A., I, 374.

Ethylene compounds of platinum. A. GELMAN (Sci. Rep. Leningrad State Univ., 1936, 2, No. 2, 5—47).—C₂H₄ is passed through aq. K₂PtCl₄ for 15 days at room temp., and aq. Pt(NH₃)₄Cl₂ is added, when [Pt₂C₂H₄Cl₃][Pt(NH₃)₄] is pptd. This reacts with K₂PtCl₄ to yield K[Pt₂C₂H₄Cl₃]₂·H₂O (I), identical with that obtained by Zeise from Na₂PtCl₄ and EtOH. [Pt₂C₂H₄NH₃Cl₃] reacts with HCl to afford NH₄[Pt₂C₂H₄Cl₃], and with CS(NH₂)₂ (II) to give PtCl₂·4(II) (III), indicating its *cis* configuration. An attempted prep. of the *trans*-isomeride by Jörgensen's method was unsuccessful. (I) in dil. HCl and C₅H₅N yield *cis*-[Pt₂C₂H₄C₅H₅NCl₃] (IV), converted by HCl into C₅H₅NH[Pt₂C₂H₄Cl₃], by (II) into (III), and by excess of C₅H₅N into *trans*-[Pt(C₅H₅N)₂Cl₂]. (I) and [Pt(C₅H₅N)₄]Cl₂ give [Pt₂C₂H₄Cl₃][Pt(C₅H₅N)₄]. The salts [Pt₂C₂H₄(C₅H₅N)₂Br₂], C₅H₅NH[Pt₂C₂H₄Br₃], and [Pt₂C₂H₄Br₃]₂[Pt(NH₃)₄] are described. The stability of salts of the series [Pt₂C₂H₄R₂X₂] rises in the series R = (II) < NEt₃ < C₅H₅N < quinoline, and X = CN < CNS < NO₂ < I < Br < Cl. R. T.

Inertness of cyclopentane hydrocarbons with respect to dehydrogenation catalysis. E. M. TARASOVA (Sci. Rep. Moscow State Univ., 1934, No. 3, 173—182).—2-Methylcyclopentanone and MgEtI yield *cis*-*trans*-1-methyl-2-ethylcyclopentan-2-ol, b.p. 55—61°/11 mm., converted by distillation from anhyd. H₂C₂O₄ into a mixture of 1-methyl-2-ethyl- Δ^1 - and - Δ^2 -cyclopentene (*cis*-*trans*), from which

1-methyl-2-ethylcyclopentane (I) is obtained by hydrogenation. 1-Methyl-2-*n*-propylcyclopentane (II) is prepared analogously from 1-methyl-2-*n*-propyl- Δ^2 -cyclopentene, b.p. 144–148°. (I), (II), and ethyl-, *n*-propyl-, and *n*-butyl-cyclopentane are not dehydrogenated by passage over C-Pt in H₂ or CO₂ at 300°. Under similar conditions, 1:4-dimethylcyclohexane yields *p*-xylene. (I) and Br in presence of AlBr₃ yield tetrabromo-*p*-xylene. R. T.

Estimation of cyclopentadiene and indene and their polymerisation in carbon tetrachloride solution. D. L. HAMMICK and (MISS) D. LANGRISH (J.C.S., 1937, 797–801).—cyclopentadiene (I) and indene (II) can be determined in dil. (up to 0.05*M*) solution in CCl₄ with Br in CCl₄; polymerisation of (I) in CCl₄ is bimol., and much faster than that of (II), the rate of polymerisation of both in CCl₄ being retarded by MeCN and stopped in pure MeCN or CCl₄ without O₂. The polymerisations are considered to be autoxidation processes. J. D. R.

Influence of substituents on the velocity of catalytic dehydrogenation of cyclohexane derivatives. II. A. A. BALANDIN and N. I. SCHUJIKIN (Sci. Rep. Moscow State Univ., 1936, No. 6, 281–286).—The velocity of dehydrogenation of methylcyclohexane at 200–250° (Ni-Al₂O₃ catalyst) is slightly > that of cyclohexane. R. T.

Influence of solvent on the course of chemical reactions. XIV. Aromatic hydrocarbons. K. LAUER [with Y. ABIKO] (Ber., 1937, 70, [B], 1127–1133).—Measurements are recorded of the dissociation consts. of PhOH and α - and β -C₁₀H₇-OH in H₂O by colorimetric determination of [H⁺] in partly neutralised solutions and of these and 1- and 2-anthrol in 25 vol.-% EtOH with thymolphthalein as indicator. Determinations are also based on solubility. The dipole moments of the anthrols have been measured in C₆H₆. The simple aromatic phenols differ slightly but appreciably in electrolytic dissociation, the extent of which corresponds conversely with the dipole moment. The product dissociation const. \times (dipole moment)² is const. The cause of the relationship is the polarisability of aromatic hydrocarbons which causes the formation of cationoid positions in the polynuclear members. In the cases of C₁₀H₈ and anthracene the influence of cationoid polarity on the properties of substituents can be studied without interference from effects due to the surrounding field. H. W.

Isomerisation of *m*-xylene and hexahydro-*m*-xylene during bromination. R. J. LEVINA (Sci. Rep. Moscow State Univ., 1936, No. 6, 267–268).—The chief product of bromination of *m*-xylene or hexahydro-*m*-xylene in presence of AlBr₃ is tetrabromo-*p*-xylene. R. T.

Bromination of aromatic compounds in presence of beryllium and ether. R. PAJEAU (Compt. rend., 1937, 204, 1202–1204).—Be, Br, and Et₂O form a loose complex, BeBr₂(Et₂O)₂ (I), which catalyses brominations as follows. C₆H₆ gives *p*-C₆H₄Br₂, alkylbenzenes give tribromoalkylbenzenes, dialkylbenzenes give tetrabromodialkylbenzenes, Ph₂ yields 4:4'-dibromodiphenyl, CH₂PhCl yields *p*-

C₆H₄Br·CH₂Br, and dihydric and alkyl-phenols yield Br₄-derivatives. Bromination of PhOH and nitrophenols is not affected by (I), and proceeds normally. J. D. R.

Metal halide catalysts for hydrocarbon reactions. A. V. GROSSE and V. N. IPATIEV (J. Org. Chem., 1937, 1, 559–566).—C₂H₄ ethylates C₆H₆ (up to C₆Et₆) in presence of HCl and the following salts, the figures being the no. of mols. of C₂H₄ reacting at the stated temp./>1 atm. in presence of 1 mol. of salt: BeCl₂, 200° 50, BF₃, 25° 35, AlCl₃, 75° 75, TiCl₄, 170° 5, ZrCl₄, 100° 90, NbCl₅, 75° 25, TaCl₅, 75° 60, HfCl₄, ThCl₄, EtCl₅. Reaction is by way of EtCl, for, if much HCl is used, EtCl is detected in the product. R. S. C.

Polymerisation of styrene as revealed by the Raman effect.—See A., I, 283.

Kinetics of polymerisation reactions.—See A., I, 366.

Thermal polymerisation reactions.—See A., I, 366.

Mechanism of thermal polymerisation and polycondensation.—See A., I, 366.

Chlorobromide of styrene. E. URION and L. NAMIAS (Bull. Soc. chim., 1936, [v], 3, 2333–2337).—Styrene (I) when treated with an equimol. mixture of Cl₂ and Br gives about 10% of CHPhCl·CH₂Cl, about 20% of CHPhBr·CH₂Br (II), and 65–70% of α -chloro- β -bromoethylbenzene (III), m.p. 27.5–28°, which with cold KOH-EtOH gives α -chlorostyrene, b.p. 73°/16 mm., hydrolysed to CPhMe. The rate of addition of BrCl to (I) is of the same order as that of Cl₂ and Br. The fusion diagram of (II) and (III) is given. H. G. M.

Action of diazo-compounds on unsaturated compounds. Determination of mono- and polymeride of phenylbutadiene. A. P. TERENTIEV and M. E. ZEGELMAN (Sci. Rep. Moscow State Univ., 1936, No. 6, 257–261).—CHPh·CH·CH₂·CH₂ (I), but not its dimeride, combines with diazotised *p*-NO₂-C₆H₄-NH₂. The reaction of polymerisation is one of the second order. C₆H₅N reacts with (I), and is not a suitable solvent for studying velocity of polymerisation. R. T.

Nitronic ester of phenylcyanonitromethane. F. ARNDT, L. LOEWE, and H. İŞİK (Rev. Fac. Sci. Istanbul, 1937, 2, 139–141).—CN·CPh·NO·OAg and MeI give the *O*-Me ether (I), m.p. 40–41°, also obtained from CN·CPh·NO₂H and CH₃N₂ in Et₂O. Contrary to Hantzsch (A., 1907, i, 500) (I) decomposes at 90°. (I) with HI-AcOH liberates 2 I and is converted into CN·CPh·N·OH. J. W. B.

Units of affinity of the elements. J. GNEZDA (Separate, Zagreb, 1937, 17 pp.; cf. A., 1933, 450).—In accord with the author's theory, when CHPh₃ is kept for 3 months in excess of PhMe, the compound, C₄₀H₃₇ (= CHPh₃ + 3PhMe – 3H), m.p. 90–93°, is formed. With mesitylene, CHPh₃ yields a similar compound, C₂₈H₂₅, m.p. 91–93.5°. The theory also indicates that 8 Cl- and 10 Hg-“viravals” remain unsaturated in HgCl₂, and this is said to explain the existence of certain additive compounds. The effects

(II) absorbs Br in cold CS₂ and the product loses HBr when distilled and gives 1-chloro-2-bromoindene (III), b.p. 115°/0.1 mm., the constitution of which is established by its ozonisation to homophthalic acid. With Br in CS₂ (III) affords some 1:2-dibromoindene (IV), m.p. 133°, which is resistant towards Br. (I) and PBr₅ similarly afford 1-bromoindene, m.p. 42°, and some (IV). H. W.

Synthesis of 1:2:4-trimethyl-7-isopropylindene. W. G. WHITTLESTON (J. Amer. Chem. Soc., 1937, 59, 825—826).—*p*-Cymene, 40% CH₂O (not paraformaldehyde), ZnCl₂, and, best, a little NiCl₂, and gaseous HCl at 60° give 2-methyl-5-isopropylbenzyl chloride, b.p. 123—124°/20 mm., and thence by standard methods Et₃ 2-methyl-5-isopropylbenzylmalonate, b.p. 190—195°/9 mm., the corresponding acid, m.p. 165°, β-*p*-cymylpropionic acid, b.p. 190—195°/20 mm., m.p. 76.5°, 2-methyl-5-isopropylbenzylmethylmalonic acid, cryst., β-*p*-cymylisobutyric acid, b.p. 189—190°/12 mm., 2:4-dimethyl-7-isopropylhydrindone, b.p. 147—150°/9 mm., and (by MgMeI) 1:2:4-trimethyl-7-isopropylindene, b.p. 140—145° (slight decomp.)/10 mm., m.p. 99.5° (picrate, m.p. 88—89°). R. S. C.

Decomposition of tetralin peroxide. IV. Effect of sulphur and sulphur compounds.—See A., I, 316.

Irreversible catalysis of unsaturated cyclic hydrocarbons. Contact transformation of Δ²-octahydronaphthalene. M. B. TUROVA-POLLAK (Sci. Rep. Moscow State Univ., 1934, No. 3, 193—196).—*trans*-Δ²-Octahydronaphthalene (I) yields C₁₀H₈ and *trans*-decahydronaphthalene when passed over Pd-asbestos at 200—205° in CO₂. *trans*-2-Hydroxydecahydronaphthalene yields (I) when heated with NaHSO₄ at 180—200° (3 hr.), and the *cis*-isomeride when heated with ZnCl₂. R. T.

Δ⁹:10-Octahydronaphthalene. Isomerising action of zinc chloride in dehydration of 2-cyclopentylcyclopentanol. N. I. SCHUJKIN (Sci. Rep. Moscow State Univ., 1934, No. 3, 197—202).—2-cyclopentylcyclopentanol and ZnCl₂ (180°; 2 hr.) yield Δ¹:9- and Δ⁹:10-octahydronaphthalene (I), which with HBr yields 9-bromodecahydronaphthalene, and this yields pure (I) when boiled with EtOH-KOH. R. T.

Dehydrogenation catalysis of condensed ring hydrocarbons. I. N. TITZ and G. J. BERGO (Sci. Rep. Moscow State Univ., 1936, No. 6, 353—357).—Di- and octa-hydroanthracene yield anthracene when passed over C-Pt at 310°. Acenaphthene is not dehydrogenated under these conditions. R. T.

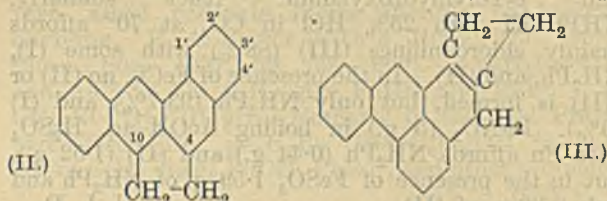
Action of aluminium chloride on octahydroanthracene. S. E. MICHLINA (Sci. Rep. Moscow State Univ., 1934, No. 3, 209—212).—The products obtained by distilling octahydroanthracene from AlCl₃ are tetradeca-hydroanthracene and tetrahydronaphthalene; the production of butadiene is postulated. R. T.

Friedel-Crafts reaction between oxalyl chloride and 1:2-benzanthracene. A. DANSI (Gazzetta, 1937, 67, 85—88).—This reaction in CS₂ gives 1:2-benzanthracene-10-carboxylic acid, m.p. 220°, with

4:10-oxalyl-1:2-benzanthracene, m.p. 230—234°. The latter is oxidised (KMnO₄) and esterified (Ag salt and MeI) to Me₂ anthraquinone-1:2:4-tricarboxylate, m.p. 193°, and reduced (distillation in H₂ over Zn) to 4:10-dimethylene-1:2-benzanthracene, m.p. 130°.

E. W. W.

4:10-Ace-1:2-benzanthracene. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1937, 59, 883—887).—γ-Keto-γ-5-hydrindylbutyric acid (from hydrindene, succinic anhydride, and AlCl₃ in C₂H₅Cl-PhNO₂), m.p. 125—125.5°, with Zn-Hg in HCl-PhMe gives γ-5-hydrindylbutyric acid, m.p. 54.9—55.2°, the chloride, b.p. 170°/10 mm., of which with AlCl₃ in CS₂ gives 6:7-trimethylene-1-keto-1:2:3:4-tetrahydronaphthalene, b.p. 151—152°/2 mm., the structure of which is proved by oxidation to pyromellitic acid. Clemmensen reduction affords 6:7-trimethylenetetrahydronaphthalene, b.p. 104—106°/3 mm., which with BzCl gives 5-benzoyl-6:7-trimethylenetetrahydronaphthalene (I), b.p. 183—185°/0.5 mm., converted by Se at 290° in N₂ into impure 1-benzoyl-2:3-trimethylenenaphthalene, b.p. 215—220°/1.5 mm., which at 405° yields 4:10-ace-1:2-benzanthracene (II), m.p. 138.5—140° (picrate, m.p.



148—149°). CrO₃-oxidation of (II) gives 1:2-benzanthraquinone-4-acetic acid, m.p. 228—229.5°. When heated at 410° (I) affords 17—21% of (?) Δ³-dehydro-3:4-trimethylene-2-isobenzanthrene (III), m.p. 144.5—145° (picrate, m.p. 136—137°; oxidised to phenanthrene-8:9-dicarboxylic anhydride), and 4% of 1':2':3':4'-tetrahydro-4:10-ace-1:2-benzanthracene, m.p. 106—107° (picrate, m.p. 131—132°), dehydrogenated to (II) by Se. M.p. are corr. R. S. C.

Derivatives of pyrene. G. LOCK (Ber., 1937, 70, [B], 926—930).—Stepwise bromination of pyrene (I) is possible in CCl₄. 3-Bromopyrene, m.p. 95° [picrate, m.p. 172° (corr.)], is thus obtained. Its constitution is established by its conversion by CuCN in boiling quinoline into 3-cyanopyrene, m.p. 151.5° [picrate, m.p. 141° (corr.)], which is transformed by MgPhBr in Et₂O-C₆H₆ into 3-benzoylpyrene (picrate, m.p. 159°), identical with that described by Scholl and Seer (A., 1913, i, 58). Further bromination of (I) affords dibromopyrenes, m.p. 221—222° (corr.) and 176—177° (corr.), respectively, probably 3:8- and 3:10-derivatives. H. W.

Pyrene series. K. DZIEWOŃSKI and L. STERNBACH (Bull. Acad. Polonaise, 1937, A, 81—85).—Acetylation of pyrene (AlCl₃) yields 3-acetylpyrene (I), m.p. 94° (picrate, m.p. 160°; phenylhydrazone, m.p. 168°), the oxime of which, m.p. 198°, is converted by HCl in Ac₂O into 3-acetamidopyrene, m.p. 260°, hydrolysed to 3-aminopyrene. (I) when heated with S yields bis-4:3-pyrenethiophenindigo, m.p. > 400°, and with MgMeI followed by hydrolysis gives

3-isopropenylpyrene, m.p. 61.5—62.5° (*picrate*, m.p. 146—147.5°). A. LI.

Catalytic condensation of acetylene with aromatic amines. X. Intermediate products of condensation of acetylene with amines. N. KOZLOV and O. SERKO. XI. Condensation of acetylene with aniline in presence of mercury salts. N. KOZLOV and G. RODMAN (J. Gen. Chem. Russ., 1937, 7, 832—835, 836—838).—X. C_2H_2 and NH_2Ph in presence of $HgCl_2$ yield Schultz's and Eckstein's bases; $NPh:CHMe$ is supposed to be an intermediate stage in their production.

XI. The above reaction may be catalysed by $HgSO_4$, Hg_2SO_4 , or $HgNO_3$, but not by $Hg(CN)_2$. R. T.

Oxidation reaction occurring during reduction of aromatic nitro-compounds. K. G. MIZUTSCH (Compt. rend. Acad. Sci. U.R.S.S., 1937, 15, 37—40; cf. A., 1936, 601).— $NHPh:OH$ with warm aq. H_2SO_4 in CO_2 atm. affords azoxybenzene (I) and NH_2Ph , but mainly (85%) $p-NH_2-C_6H_4-OH$ (II). In the presence of $FeSO_4$, very little (II) is formed; NH_2Ph (68%) and (I) (30%) are the main products. *o*- and *p*-Tolylhydroxylamine react similarly. $NHPh:OH$ with 25% HCl in CO_2 at 70° affords mainly chloroanilines (III) (88%) with some (I), NH_2Ph , and (II). In the presence of $FeCl_2$, no (II) or (III) is formed, but only NH_2Ph (93.7%) and (I) (6%). $PhNO_2$ (5 g.) in boiling $AcOH$ -aq. H_2SO_4 with Sn affords NH_2Ph (0.44 g.) and (II) (1.52 g.), but in the presence of $FeSO_4$ 1.59 g. of NH_2Ph and only 0.30 g. of (II). J. L. D.

Condensations of aromatic amines with formaldehyde in media containing acid. VII. Polymeric states and structures of some anhydro-*p*-alkylaminobenzyl alcohols. W. S. YOUNG and E. C. WAGNER (J. Amer. Chem. Soc., 1937, 59, 854—855; cf. this vol., 308).—The compounds ($-NR-C_6H_4-CH_2-$)_n, in which $R = Me$, m.p. 209—212°, *Et*, m.p. 84—86°, *Pr*^a, m.p. 106—108°, *Bu*^a, m.p. 52—53°, *isoamyl*, m.p. 46—48°, and CH_2Ph , m.p. 162—163°, are found by cryoscopy to be trimeric in C_6H_6 (cf. Friedländer, A., 1903, i, 252). Much higher mol. wts. are found in camphor. The bases and, to a smaller extent, their hydrochlorides, are unstable. Structures are confirmed by reduction by $Zn-H_2SO_4$ to the base, $NHPhR$. M.p. are corr. R. S. C.

Action of primary aromatic amines on 1:6-dichlorodiethylenediamminocobaltic chloride. A. ABLOV (Bull. Soc. chim., 1936, [v], 3, 2270—2279; cf. A., 1936, 1241).—The following compounds have been obtained by interaction of praseo-I: 6-dichlorodiethylenediamminocobaltic chloride (I) with the appropriate primary aromatic amine, all of which have a dissociation const. in H_2O < that of NH_2Ph : $[Co en_2(m-C_6H_4Me-NH_2)Cl]X_2$ [$en = (CH_2NH_2)_2$; $X = Cl, Br, I$, and NO_3]; $[Co en_2(o-NH_2-C_6H_4-OMe)Cl]X_2 \cdot 2H_2O$ ($X = Cl, Br$, and I ; the nitrate has only 1 H_2O); $[Co en_2(o-NH_2-C_6H_4-OEt)Cl]X_2 \cdot 2H_2O$ ($X = Cl$ and Br); $[Co en_2(p-NH_2-C_6H_4-OMe)Cl]X_2$ ($X = Br, I$, and NO_3 ; the chloride has 1 H_2O); $[Co en_2(p-NH_2-C_6H_4-OEt)Cl]Cl_2 \cdot H_2O$ (the correspond-

ing nitrate has no H_2O); $[Co en_2(p-NH_2-C_6H_4F)Cl]X_2$ ($X = Br, I$, and NO_3 ; the chloride has 1 H_2O). Primary aromatic amines [$o-C_6H_4Me-NH_2$, $p-C_6H_4Cl-NH_2$, $o-C_6H_4(NH_2)_2$] with a dissociation const. < that of NH_2Ph cause isomerisation of (I) into the violeo-chloride. H. G. M.

Carbamide derivatives in the alkanolamine series. R. W. CHARLTON and A. R. DAY (J. Org. Chem., 1937, 1, 552—558).—The following carbamides are prepared from the appropriate alkanolamine with $NH_2 \cdot CO \cdot NH \cdot NO_2$ in H_2O or $\alpha-C_{10}H_7 \cdot NCO$ in Et_2O or dioxan: β -hydroxyethyl- (I), m.p. 94—95° [*O*-*p*-nitro- (II), m.p. 183—184°, and *p*-amino-benzoate (III), m.p. 203°; *ON*-dicinnamoyl derivative, m.p. 173.5—174° (absorbs 2 H_2 catalytically)]; β -hydroxy-*n*-propyl-, m.p. 119° (mixed mono- and di-*p*-nitro-benzoyl, m.p. 182—186°, *ON*-di-*p*-aminobenzoyl, m.p. 210—211°, *O*-*p*-aminobenzoyl, m.p. 149—150°, and *ON*-dicinnamoyl derivative, m.p. 179—179.5°); *NN*-di- β -hydroxyethyl- (*OO*-di-*p*-nitro-, forms, m.p. 140—140.5° and 152—153°, and *p*-amino-benzoate, m.p. 172.5—172.8°); *N*- α -naphthyl-*N'*- β -hydroxyethyl- (IV), m.p. 186° [*O*-*p*-nitro-, m.p. 191° (decomp.), and *p*-amino-benzoate (V), m.p. 193—193.5° (decomp.)], *N*- α -naphthyl-*N*- β -hydroxy-*n*-propyl-, m.p. 162° [*O*-*p*-nitro-, m.p. 218—221° (decomp.), and *p*-amino-benzoate, m.p. 171°], and *N*- α -naphthyl-*N'*-di- β -hydroxyethyl-carbamide, m.p. 126—127°. α -Dicarb-amido-, + H_2O , m.p. 86—87°, α -di-1-naphthylcarb-amido-propan- β -ol, m.p. 171.5—172°, and 6-carbamido-thymol, m.p. 179°, were also made. M.p. are corr. The structure of the *O*-esters is indicated by their failure to react with Na in C_6H_6 or $PhMe$ and by the fission of (II) by NH_3-EtOH at 100° to *p*- $NO_2-C_6H_4-CO \cdot NH_2$. (I), (III), (IV), and (V) are weak hypnotics; (II) and (IV) are toxic. R. S. C.

Influence of reaction conditions on the yields of isomerides in nitration of acetanilide. A. P. TERENTIEV and B. M. KEDROV (Sci. Rep. Moscow State Univ., 1936, No. 6, 213—234).—The content of *o*- $NO_2-C_6H_4 \cdot NH_2$ (I) in the product of nitration of $NHPhAc$ rises from 6—7% when 100% H_2SO_4 is taken to 28% with 84% H_2SO_4 ; nitration does not proceed when the H_2SO_4 contains >16% of H_2O , whilst the use of 10% oleum leads to production of tarry products. Increasing the amount of 100% H_2SO_4 taken per g. of $NHPhAc$ from 2 to 5 ml. greatly lowers the yield of (I), but further addition of H_2SO_4 does not further reduce it. The yield of (I) is slightly increased by raising the nitration temp. from -3° to 10° , whilst further rise to 40° has no effect. The *m*- $NO_2-C_6H_4 \cdot NH_2$ content of the product is independent of temp., concn. and amount of H_2SO_4 taken. Addition of $AcOH$ or $HgSO_4$ does not affect the relative yields of (I) and *p*- $NO_2-C_6H_4 \cdot NH_2$. R. T.

Manufacture of aminomethylnaphthalene-sulphonic acids.—See B., 1937, 420.

Manufacture of [sugar] derivatives of *o*-nitro-anilines and *o*-phenylenediamines.—See B., 1937, 420.

Optically active tricyclohexanediaminecobaltic salts and ethylenediaminecyclohexanediaminecobaltic salts.—See A., I, 289.

Diaryls and their derivatives. XIII. Azodyes from 6:6'-diamino-2:2'-dihydroxy-1:1'-dinaphthyl. J. S. JOFFE (J. Gen. Chem. Russ., 1937, 7, 1022—1025).—2- β -Hydroxynaphthaleneazo-, m.p. 292°, and 2-(2''-hydroxy-3''-carboxynaphthalene)-azo-6:2':6'-trihydroxy-1:1'-dinaphthyl are prepared by coupling with diazotised 6:6'-diamino-2:2'-dihydroxy-1:1'-dinaphthyl. R. T.

Action of mixed organo-magnesium compounds on the phenylhydrazones of aliphatic aldehydes. Preparation of *s*-alkylphenylhydrazines. P. GRAMMATICAKIS (Compt. rend., 1937, 204, 1262—1263; cf. A., 1936, 837).—CH₃Et·N·NHPh (I) with MgPhBr affords *N*-phenyl-*N'*- α -phenylpropylhydrazine, also obtained from CHPh·N·NHPh and MgEtBr. (I) with MgEtBr gives *N*-phenyl-*N'*- α -ethylpropylhydrazine, b.p. 138°/12 mm. [hydrochloride, m.p. 185° (decomp.); Ac derivative, m.p. 93°; PhNCO derivative, m.p. 104°]. CHMe·N·NHPh with MgPhBr similarly affords *N*-phenyl-*N'*- α -phenylethylhydrazine, b.p. 190°/12 mm. [hydrochloride, m.p. 202° (decomp.); Ac derivative, m.p. 118°; PhNCO derivative, m.p. 187°], and with MgEtBr gives *N*-phenyl-*N'*- α -methylpropylhydrazine, b.p. 136°/12 mm. [hydrochloride, m.p. 195° (decomp.); Ac derivative, b.p. 177°/10 mm.; PhNCO derivative, m.p. 139°]. CH₂·N·NHPh with MgPhBr affords CH₂Ph·NH·NHPh. These hydrazines are oxidised in air to hydrazones. J. L. D.

Isomeric di- and tri-nitrophenylhydrazones. H. BREDERECK and E. FRITZSCHE (Ber., 1937, 70, [B], 802—809; cf. A., 1933, 154).—Further examples of isomeric di- and tri-nitrophenylhydrazones are given and reasons are advanced for considering them due to *cis-trans* isomerism. 5-Ethoxymethylfurfuraldehyde is converted by 2:4:6-(NO₂)₃C₆H₃·NH·NH₂ in boiling EtOH containing conc. HCl into 5-ethoxymethylfurfuraldehyde-2:4:6-trinitrophenylhydrazone, (I) m.p. 176—178°, (II) m.p. 152—154°. Interconversion occurs when (I) or (II) is boiled in AcOH. 5-Methoxymethylfurfuraldehyde-2:4:6-trinitrophenylhydrazone exists in two forms, m.p. 180—182° and 165—167°, respectively. Protracted treatment of (I) with boiling AcOH—Ac₂O yields 5-acetoxymethylfurfuraldehyde-2:4:6-trinitrophenylhydrazone, forms m.p. 198—199° and 205—207°, respectively. Isomeric forms are not obtained in the cases of furfuraldehyde-2:4:6-trinitrophenylhydrazone, m.p. 244—246°, or *o*-nitrophenylhydrazone, m.p. 155—156°, 5-ethoxymethylfurfuraldehyde-*o*-nitrophenylhydrazone, m.p. 127—129°, furfuraldehyde-2:4-dinitrophenyl-*N*-methylhydrazone, m.p. 187—189°, 5-ethoxymethylfurfuraldehyde-2:4:6-trinitrophenyl-*N*-methylhydrazone, m.p. 116—118°, pyrrole-2-aldehyde-2:4-dinitrophenylhydrazone, m.p. 283—286° or thiophen-2-aldehyde-2:4-dinitrophenylhydrazone, m.p. 233—236°. Pyromucyl chloride gives pyromuc-2:4-dinitrophenylhydrazone, m.p. 211—212°, or pyromuc-2:4-dinitrophenyl-*N*-furoylhydrazide, m.p. 195—197°. Pyromuc-2:4-dinitrophenyl-*N*-methylhydrazide has m.p. 177—179°. H. W.

Alkylation of phenols with alcohols in presence of aluminium chloride. II. Alkylation with sec.- and *n*-alcohols. I. P. TZUKERVANIK and Z. N.

NAZAROVA (J. Gen. Chem. Russ., 1937, 7, 623—631).—The following alkylphenols are obtained in good yield by heating the phenol with alcohols in presence of 2 mols. of AlCl₃ per mol. of alcohol: *p*-C₆H₄Pr^{*o*}·OH, *o*- and *p*-C₆H₄Pr^{*o*}·OMe, and 1:3:6-C₆H₃MePr^{*o*}·OH, with Pr^{*o*}OH in light petroleum at 110—120°, *p*-CHMeEt·C₆H₄·OH, *p*-CHMeEt·C₆H₄·OMe, and *di*-sec.-butylanisole, b.p. 140—142°/11 mm., with CHMeEt·OH in ligroin at 140—150°, CHEt₂·C₆H₄·OH, and *o*-, b.p. 140—150°/30 mm., and *p*- α -methylbutylphenol, b.p. 150—156°/30 mm., from PhOH and CHMePr·OH (I) (50°; 4 hr.), sec.-amyl-, b.p. 223—230°, and *di*-sec.-amyl-anisole, b.p. 245—260°, from PhOMe and (I), C₆H₅Et₂·OH, *o*- and *p*-C₆H₄Et·OH, and *o*- and *p*-C₆H₃Et₂·OH, from PhOH and EtOH (120—140°; 6 hr.), *o*- and *p*-C₆H₄Pr^{*o*}·OH from PhOH and Pr^{*o*}OH, *o*- and *p*-C₆H₄Bu^{*o*}·OH and C₆H₃Bu₂·OH, from Bu^{*o*}OH and PhOH, C₆H₄Bu^{*o*}·OH from Bu^{*o*}OH and PhOH, and a mixture of amylphenols from *iso*-C₅H₁₁·OH and PhOH. By-products of the type C₆H₄R·OR are obtained in all cases; they are readily converted into alkylphenols by boiling. R. T.

Migration of alkyl radicals. I. Transfer of *tert.* alkyl radicals from phenols to hydrocarbons. R. A. SMITH [with J. ROSEN] (J. Amer. Chem. Soc., 1937, 59, 899—900).—*p*-C₆H₄Bu^{*o*}·OH and AlCl₃ in hot C₆H₆ give PhOH and PhBu^{*o*}. *p*-CMe₂Et·C₆H₄·OH gives similarly in the cold PhOH and CPhMe₂Et. *p*-CH₂Bu^{*o*}·CMe₂·C₆H₄·OH in cold or hot C₆H₆ yields PhOH, PhBu^{*o*}, and other products. R. S. C.

2:6-Dipropylcyclohexanols. G. VAVON and P. ANZIANI (Bull. Soc. chim., 1937, [v], 4, 1080—1084).—2:6-Diallylphenol (cf. A., 1919, i, 266) with H₂—Pt gives 2:6-dipropylphenol and then, with H₂—Pt in AcOH, *cis-cis*-2:6-dipropylcyclohexanol (I), b.p. 119—120°/13 mm. (*H* phthalate, m.p. 95°; *H* succinate, m.p. 40°; phenylcarbamate, m.p. 95°), oxidised by CrO₃ to 2:6-dipropylcyclohexanone (II) (cf. A., 1932, 161). (II) with Na—EtOH affords *cis-trans*-2:6-dipropylcyclohexanol (III), m.p. 113° (phthalate, m.p. 160—163°; *H* phthalate, m.p. 87—88°; *H* succinate, m.p. 85°; phenylcarbamate, m.p. 150°). Ethers of (I) are hydrolysed less rapidly than those of (III) and hence have the *cis* configuration. (I) when heated with Na at 200° is partly converted into (III). J. L. D.

Oxidation of substituted phenols. Effect of iodine in the *o*- and *p*-positions. G. H. WOOLLETT, F. M. DAVIS, C. N. JONES, and (Miss) M. NEILL (J. Amer. Chem. Soc., 1937, 59, 861—864).—*p*-I hinders, but does not entirely prevent, formation of diphenylquinones by oxidation of 2:6-substituted phenols; the % reduction of yield is approx. const. for different phenols. The formation of 3:5:3':5'-tetraiododiphenyl-4:4'-quinone (I) from C₆H₃I₄·OH and K₃Fe(CN)₆ is confirmed by reduction (N₂H₄) of the product to 3:5:3':5'-tetraiodo-4:4'-dihydroxydiphenyl, m.p. 284° (decomp.), which re-forms (I) with CrO₃ or FeCl₃; it amounts to 2.1% of the crude product. 2:6-C₆H₃I₂·OH and CrO₃ give 31% of (I). 2:6-(NHBr)₂C₆H₃·OH and HIO₃, KMnO₄, or, best, NaNO₂ in AcOH, give 84% of 3:5:3':5'-tetrabenz-

amidodiphenyl-4:4'-quinone (II), *cryst.* 4-Iodo-2:6-dibenzamidophenol [from $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{OH}$], m.p. 232° (decomp.) [Bz derivative, m.p. 253—254° (decomp.)], and CrO_3 give 11.3% of (II). R. S. C.

Decomposition of ethers with sodium in liquid ammonia. P. SCHORIGIN and S. A. SKOBLINSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 505—508).—With Na in liquid NH_3 , *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OCPh}_3$ yields *o*-cresol and CHPh_3 , $\text{CH}_2\text{Ph}\cdot\text{OPh}$ gives PhOH and dibenzyl, and Ph_2O affords PhOH. Diisomyl ether is not attacked in 5½ days. J. D. R.

Diazo coupling of 5-hydroxy-6-methylhydrindene. L. F. FIESER and W. C. LOTHROP (J. Amer. Chem. Soc., 1937, 59, 945).—The statement that 5-hydroxy-6-methylhydrindene does not couple (A., 1936, 1503) is incorrect; the *p*-nitrobenzeneazo-, m.p. 230—232°, and benzeneazo-, m.p. 141—143°, compounds are obtained in moderate yields in slightly, but in minute yields in conc., alkaline solution. R. S. C.

Manufacture of sulphonic acids of 3-hydroxy-acenaphthene.—See B., 1937, 420.

Manufacture of 3:4:5:6-tetrahalogeno-aminophenols.—See B., 1937, 420.

Synthesis of iretol. R. E. DAMSCHRODER and R. L. SHRINER (J. Amer. Chem. Soc., 1937, 59, 931—933).—2:4:6-(NO_2) $_3\text{C}_6\text{H}_2\cdot\text{OMe}$ (from picryl chloride and NaOMe), *forms*, m.p. 50—51°, 56—57°, 58—59°, and (stable) 68—69°, with H_2 and very active PtO_2 or a large amount of Raney Ni in EtOH give 2:4:6-(NH_2) $_3\text{C}_6\text{H}_2\cdot\text{OMe}$, m.p. 116.5—117.5° (corr.), converted by conc. HCl into iretol [2:4:6-(OH) $_3\text{C}_6\text{H}_2\cdot\text{OMe}$], m.p. 187.5—188.5° (corr.), isolated in CO_2 and purified by sublimation in vac. R. S. C.

β -Phenyl sulphide. III. O. HINSBERG (Ber., 1937, 70, [B], 936—939; cf. A., 1936, 602).—“ β -Diphenylsulphonium hydroxide” can be obtained pure by taking advantage of its solubility in H_2O . When dried at 90° it has the probable composition, $\text{SHPh}_2\cdot\text{OH}\cdot\text{H}_2\text{O}$; it is an approx. 1:1 mixture of the α - and β -compounds. Its basic perchlorate is transformed by H_2O_2 in AcOH into a perchlorate, $\text{C}_{12}\text{H}_{17}\text{O}_9\text{S}_2\text{Cl}$, m.p. 76—78°, converted by KOH-EtOH into α - Ph_2S and β - Ph_2SO_2 . Since these are not present in the initial material, the fundamental forms are α -OH-SPh: C_6H_5 and β -OH-SPh:(C_6H_5) \angle O . The experiments explain the production of α - Ph_2S during the prep. of β - Ph_2S from purified basic perchlorate. H. W.

Pinacol rearrangement of *cis*- and *trans*-1:2-dimethylcyclohexane-1:2-diol. Relationship of the Walden inversion to the mechanism of molecular rearrangements. P. D. BARTLETT and I. PÖCKEL (J. Amer. Chem. Soc., 1937, 59, 820—825).—*cis*-1:2-Dimethylcyclohexane-1:2-diol gives solely 2:2-dimethylcyclohexanone (74%) under conditions (20% H_2SO_4) in which the *trans*-isomeride gives 1-acetyl-1-methylcyclopentane (78%). Assuming the ring to have an average planar configuration, that group migrates which is located in space near the opposite side of $\text{C}_{(1)}$ to that occupied by the OH which

is to be replaced. This does not accord with loss of the OH before migration, nor with the “open sextet” theory; a modification of this theory is proposed. The formation of isobornyl chloride (I) and acetate without the bornylisomerides in the Wagner-Meerwein rearrangement necessitates a Walden inversion if (I) has the *exo*-structure; this is incompatible with the open sextet theory and with reaction by way of solvated carbonium ions. It is explained by a “push and pull” theory, thus: $\text{A}^+ + \text{Cl}\cdot\text{C}\cdot\text{C}\cdot\text{C} < + \text{ClA} \rightarrow \text{ACl} + >\text{C}\cdot\text{C}\cdot\text{CCl} + \text{A}^+$; the Cl-donor and acceptor may be Cl' or HCl, which leads to a reaction of the 1.5 or second order; Meerwein's kinetic results are shown to fit either of these orders better than the first order which he favoured. R. S. C.

Preparation of *d*- and *l*-isohydrobenzoin. F. EISENLOHR and L. HILL (Ber., 1937, 70, [B], 942—947).—PhCHO is electrolytically reduced by a modification of Law's method (J.C.S., 1906, 89, 512; 1907, 91, 1753) to a mixture of much hydrobenzoin (I), m.p. 139—140°, and little isohydrobenzoin (II), m.p. 121—22°, accompanied by the (?) polymorphous forms, m.p. 103° and 93°, respectively. Gradual addition of Br to (I) and yellow P in CS_2 affords α -stilbene dibromide, transformed by KOAc in AcOH into (II). (II) is separated into its optical antipodes by selection of the crystals formed when its solution in Et_2O is allowed to evaporate slowly. *d*-isoHydrobenzoin has $[\alpha]_D^{25} +95.46^\circ$ ($c = 1.598$), $[\alpha]_D^{20} +94.0^\circ$ ($c = 2.000$) in 96% EtOH, $[\alpha]_D^{25} +122^\circ$ in C_6H_6 , whilst the *l*-form has $[\alpha]_D^{25} -96.54^\circ$ ($c = 1.6004$), $[\alpha]_D^{20} -93.5^\circ$ ($c = 2.000$) in 96% EtOH, $[\alpha]_D^{25} -122^\circ$ in C_6H_6 . H. W.

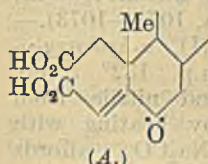
Hydrogenation of acetylenic compounds. XXVII. Hydrogenation of *s*-diphenylditolylbutinenediol. J. S. SALKIND and E. E. MARTINSON (J. Gen. Chem. Russ., 1937, 7, 815—817).—COPh: $\text{C}_6\text{H}_4\text{Me}$ -*p* and $(\text{C}\cdot\text{MgBr})_2$ yield $\alpha\delta$ -diphenyl- $\alpha\delta$ -di-*p*-tolyl- Δ^8 -butinene- $\alpha\delta$ -diol, m.p. 146°, which yields $\alpha\delta$ -diphenyl- $\alpha\delta$ -di-*p*-tolylbutane- $\alpha\delta$ -diol, m.p. 176°, when hydrogenated in presence of Pt, and *cis*-, m.p. 96°, and *trans*- $\alpha\delta$ -diphenyl- $\alpha\delta$ -di-*p*-tolyl- Δ^8 -butene- $\alpha\delta$ -diol, m.p. 188—190°, in presence of Pd catalyst. R. T.

Enzymic hydrogenation of unsaturated compounds.—See A., III, 219.

Synthesis of vitamin-A. R. KUHN and C. J. U. R. MORRIS (Ber., 1937, 70, [B], 853—858).— β -Ionone-semicarbazone is converted by treatment with *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and steam into pure β -ionone, b.p. 128/8 mm., which is condensed with Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ to Et β -ionylideneacetate, b.p. 162°/3 mm. Addition of this to the solution obtained by treatment of MgMeI in Et_2O with *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ affords β -ionylideneacet-*o*-toluidide (I), which is partly *cryst.* at -40° . (I) is converted by PCl_5 in C_6H_6 into the imidochloride, which is added to a suspension of CrCl_2 in Et_2O , thus giving β -ionylideneacetaldehyde (II), $\text{CH}_2\angle\text{CH}_2\text{CMe}_2\text{CMe}_2\text{CH}\cdot\text{CH}\cdot\text{CMe}_2\text{CH}\cdot\text{CHO}$, b.p. 110° (bath)/10 $^{-4}$ mm. (slight decomp.) (semicarbazone, m.p. 193—195°). (II) reduces warm $\text{Ag}_2\text{O}\cdot\text{NH}_3$ and gives a reddish-brown ppt. with SbCl_3 in CHCl_3 . Addition of $\text{CMe}_2\text{CH}\cdot\text{CHO}$ to a solution of (II) in EtOH containing piperidine and AcOH gives the aldehyde,

$\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe} \end{smallmatrix} \text{C}[\text{CH}:\text{CH}:\text{CMe}:\text{CH}]_2 \cdot \text{CHO}$, which gives a bluish-green colour with SbCl_3 in CHCl_3 and is reduced by $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH to the corresponding alcohol, the identity of which with vitamin-A is shown by the mixed chromatographic adsorption test on Al_2O_3 , and growth test on rats. H. W.

Oxidation of cholesterol with selenious acid. A. BUTENANDT and E. HAUSMANN (Ber., 1937, 70, [B], 1154—1159).—Oxidation of cholesterol with SeO_2 in Ac_2O at 105—110° gives Δ^5 -cholestene-3:4-diol diacetate (I), m.p. 165—166°, $[\alpha]_D^{20} +94.5^\circ$ in CHCl_3 , and Δ^4 -cholestene-3:6-diol diacetate (II), m.p. 131—133°, $[\alpha]_D^{20} -18.5^\circ$ in EtOH , hydrolysed respectively to 4-hydroxycholesterol (III), m.p. 174°, and Δ^4 -cholestene-3:6-diol (IV), m.p. 255—256°. The authors agree with Rosenheim and Starling (this vol., 191) in interpreting the constitution of (I) and (III) but for the following reasons do not share the view that (II) and (IV) are the *trans*-isomerides of (I) and (III). (IV) suspended in AcOH is oxidised by CrO_3 (= 6 O)



to the *ketodicarboxylic acid* (V), $\text{C}_{27}\text{H}_{42}\text{O}_5$, m.p. 185—187°, $[\alpha]_D^{20} +67.53^\circ$ in COMe_2 (Me_2 ester, m.p. 137—138° after slight softening at 135°), which must be A since it is also obtained by oxidation of Δ^4 -cholestene-3:6-dione. (V) is transformed by Zn dust in boiling AcOH into the *ketone*, $\text{C}_{26}\text{H}_{42}\text{O}_2$, m.p. 114—115°. (IV) with $\text{Al}(\text{OPr}^i)_3$ in boiling $\text{COMe}_2\text{-C}_6\text{H}_6$ gives cholestan-3:6-dione, m.p. 169°. H. W.

Unsaturated steroids. I. Constitution of cholesterolene. II. Preparation and properties of $\Delta^2:4$ -cholestadiene. III. Titration of unsaturated steroids with thiocyanogen. H. E. STAVELY and W. BERGMANN (J. Org. Chem., 1937, 1, 567—574, 575—579, 580—581).—I. Cholesterolene (I), m.p. 78—79°, $[\alpha]_D^{20} -97.5^\circ$ in CHCl_3 , prepared from cholesterol (II) by anhyd. CuSO_4 , absorbs 2 Br, but gives no cryst. bromide, absorbs 1.97 O₂ from BzO_2H , with $\text{H}_2\text{-PtO}_2$ in EtOAc gives 80% of cholestane and 20% of coprostane, and with maleic anhydride in xylene at 135° gives abnormally the acid adduct (III), $\text{C}_{31}\text{H}_{48}\text{O}_4$, decomp. 240—245°. The cholestadiene, $[\alpha]_D^{20} -112^\circ$ (IV), from *allo*- or *epiallo*-cholesterol and HCl is unaffected by $\text{Na-C}_5\text{H}_{11}\text{OH}$, is hydrogenated (PtO_2) to 85% of cholestane and 15% of coprostane, and yields (III). The dienes (I) and (IV) have the same absorption spectrum and are thus both $\Delta^3:5$ -cholestadiene. 7-Ketocholesteryl acetate and HCl-EtOH give 7-keto- $\Delta^3:5$ -cholestadiene (*semicarbazone*, m.p. 198—200°), reduced by NaOEt at 200° to $\Delta^3:5$ -cholestadiene, m.p. 78—79°, $[\alpha]_D^{20} -63.75^\circ$ in CHCl_3 , similar to the above dienes in absorption spectrum. Cholesterolenes recorded in the lit. fall into two groups with $[\alpha] -60^\circ$ to -70° and $- >100^\circ$, respectively; the nature of the isomerism is unknown.

II. When (II) and Al_2O_3 are heated at 200°/vac., a hydrocarbon, m.p. 72—74°, $[\alpha]_D^{20} -56.5^\circ$, is sometimes obtained; distillation at 240—270° gives $\Delta^2:4$ -cholestadiene (V), m.p. 63°, $[\alpha]_D^{20} +114^\circ$ in CHCl_3 , hydrogenated (PtO_2) in EtOH to coprostane only, absorbing 2 O₂ from BzO_2H , yielding with maleic

anhydride in hot C_6H_6 or, better, xylene at 135° an *isomeride*, m.p. 70—72°, $[\alpha]_D^{20} -77.8^\circ$ in CHCl_3 , and the acidic *adduct*, m.p. 268—270° (decomp.), reduced by Na-Hg to Δ^4 -cholestene, m.p. 77—78°, $[\alpha]_D^{20} +66.9^\circ$ in CHCl_3 , and rearranged by HCl-EtOH to $\Delta^3:5$ -cholestadiene. The ready change of the $\Delta^2:4$ - into the $\Delta^3:5$ -system is noted. The product, $[\alpha] +1.45^\circ$, obtained from (I) and Zn dust is probably a mixture of (I) and (V).

III. Titration with $(\text{CNS})_2$ in AcOH discloses the following no. of ethylenic linkings: cholestanone 0.1, cholesteryl chloride 0.02 and benzoate 0.05, Δ^5 -cholestene 0.1, cholestanone 0.11, sitosteryl acetate 0.04, stigmasteryl acetate 0.03, cholesterolene 0.99, $\Delta^2:4$ -cholestadiene 0.95, and ergosteryl acetate 2.03. Δ^3 , but not Δ^4 , Δ^5 , or Δ^{22} , linkings react and reaction thus indicates ethylenic linkings present in reactive positions. R. S. C.

Ether-soluble constituents of sarsaparilla root. I. J. C. E. SIMPSON and N. E. WILLIAMS (J.C.S., 1937, 733—738).—The sterol fraction on bromination of the mixed acetates gave (1) a sparingly sol. *bromoacetate*, m.p. 210—211°, debrominated to an acetate, m.p. 140—141°; free sterol, m.p. 170°, $[\alpha]_D^{17} -45.8^\circ$; *p*-nitrobenzoate, m.p. 203°, $[\alpha]_D^{17} -13.3^\circ$; *anisate*, m.p. 173.5—174.5, $[\alpha]_D^{17} -14.3^\circ$, all of which are identical with stigmasteryl and its derivatives, and (2) the filtrate, which on debromination, saponification, conversion into the 3:5-dinitrobenzoates, and fractionation from cyclohexane gave two products, (a) m.p. 207—209°, $[\alpha]_D^{17} -21.7^\circ$; corresponding free sterol, m.p. 135—135.5°, $[\alpha]_D^{17} -34.2^\circ$; acetate, m.p. 126—127°, $[\alpha]_D^{17} -34.7^\circ$; benzoate, m.p. 145—146°, $[\alpha]_D^{17} -14.2^\circ$, suggesting identity with β -sitosterol and its derivatives, (b) in minute amount, m.p. 215—217°; the free sterol, $\text{C}_{29}\text{H}_{50}\text{O}$, for which the name ϵ -sitosterol is proposed, has m.p. 143—144°, $[\alpha]_D^{17} -38.7^\circ$ (acetate, m.p. 127—128°, $[\alpha]_D^{17} -44.7^\circ$). The remaining fractions of the Honduras root consisted largely of fats, waxes, and a mixture of paraffins, m.p. 57—59°, of mean formula $\text{C}_{18}\text{H}_{38} \pm \text{CH}_2$. The non-saponifiable fraction of this mixture gave on benzylation a *substance*, m.p. 124.5—125°, apparently the dibenzoate of a dihydric phenol $\text{C}_{11}\text{H}_{14}\text{O}_3(\text{OH})_2$, which may be identical with filixic acid of male fern. With Mexican root this fraction consisted 90% of a paraffin or mixture of paraffins, m.p. 61—62°, of mean formula $\text{C}_{23}\text{H}_{48}$, 9% of a *tert*-alcohol, $\text{C}_{20}\text{H}_{42}\text{O}$, m.p. 82—82.5°, and 1% of a *substance*, $\text{C}_{29}\text{H}_{38}\text{O}_3$, m.p. 102—104°. P. W. C.

β -Estradiol. B. WHITMAN, O. WINTERSTEINER, and E. SCHWENK (J. Biol. Chem., 1937, 118, 789—795).—Reduction of α estrone ($\text{Ni-Al} + \text{NaOH}$) yields two epimeric diols, separated by pptn. with digitonin, α -estradiol, m.p. 176—178°, identical with the dihydrotheclin of MacCorquodale *et al.*, which predominates and has the greater α estrogenic activity, and β -estradiol, m.p. 220—223° (3-benzoate, m.p. 156—157°; diacetate, m.p. 139—141.5°). All m.p. are corr. A. Lx.

Silver-halogen complexes of benzoic acid. C. PRÉVOST and J. WIEMANN (Compt. rend., 1937, 204, 989—991; cf. A., 1934, 292).— AgOBz with Cl_2 , Br, or I in cold CCl_4 affords silver-halogeno-

benzoates which convert Δ^6 -heptinine into the α -halogeno-derivatives. They also react with ethylenic compounds, and with cyclohexene yield 2-chloro-, m.p. 50°, -bromo-, m.p. 64°, and -iodo-cyclohexyl benzoate, m.p. 54°.

J. L. D.

Action of thionyl chloride on aromatic amino-acids. R. GRAF and W. LANGER (J. pr. Chem., 1937, [ii], 148, 161—169).—Previous failures to obtain *N*-thionylaminobenzoyl chlorides from the NH_2 -acids and SOCl_2 (I) was due to decomp. during distillation. *o*-, *m*-, and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ with (I) give, after removal of excess of (I) at $>120^\circ$, and distillation in vac., *N*-*o*-, m.p. 31—32°, b.p. 105—106°/0.8 mm., *N*-*m*- (II), m.p. 32—33°, b.p. 140°/12 mm., and *N*-*p*-thionylaminobenzoyl chloride (III), m.p. 40—41°, these are decomposed by H_2O or by MeOH to insol. substances of high mol. wt. accompanied by the hydrochlorides of the NH_2 -acids, or of their esters. In Et_2O , with dry HCl , (II) and (III) give *m*-, decomp. about 270°, and *p*-aminobenzoyl chloride hydrochloride (IV), decomp. 250°. These are hydrolysed by H_2O , MeOH , or EtOH exclusively to the NH_2 -acid or -ester hydrochloride; with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$, (IV) gives *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{CH}_2\cdot\text{CH}_2\text{Cl}$ m.p. 86°. *p*- $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and (I) give a product which with $\text{Et}_2\text{O}\cdot\text{HCl}$ forms *p*-methylaminobenzoyl chloride hydrochloride, m.p. 168—182°. *p*-Ethyl-, m.p. 100°, *p*-*n*-propyl-, m.p. 89—90°, *p*-*n*-butyl-, m.p. 112° (decomp.), and *p*-isoamyl-aminobenzoyl chloride hydrochloride, m.p. 105° (decomp.), are similarly prepared, and converted by MeOH into the *Me* esters.

E. W. W.

Iodine value of cinnamic [acid] derivatives. A. LESPAGNOL and J. BRUNEEL (J. Pharm. Chim., 1937, [viii], 25, 454—457).— $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, its *Et*, CH_2Ph , and cinnamyl esters, and $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ have low I vals., viz., about 29, 25, 4.5—6.7, 83.3—87, and 30, respectively.

R. S. C.

cis-Cinnamic acids.—See A., I, 291.

Amido- and imido-chlorides of non-aromatic acids. X. J. VON BRAUN and H. OSTERMAYER (Ber., 1937, 70, [B], 1002—1005; cf. A., 1934, 393, 1359).—Attempts to prepare acetylenic aldehydes by a process analogous to that leading from $>\text{C}\cdot\text{CH}\cdot\text{CCl}\cdot\text{NR}$ to $>\text{C}\cdot\text{CH}\cdot\text{CHO}$ are hindered by the impossibility of avoiding addition of HCl during the action of PCl_5 on $\text{CR}\cdot\text{C}\cdot\text{CO}\cdot\text{NHR}'$. Thus, phenylpropiolanilide, m.p. 128°, is converted by PCl_5 in cold C_6H_6 into β -chlorocinnamphenylimidochloride (I), b.p. 160—170°/0.1 mm., hydrolysed by H_2O to β -chlorocinnamanilide, m.p. 133°, and transformed by NH_2Ph in Et_2O into the amidine, $\text{CPhCl}\cdot\text{CH}(\text{NPh})\cdot\text{NHPh}$, m.p. 97°. Similarly phenylpropiolethylamide, m.p. 63°, gives β -chlorocinnamethylimidochloride, b.p. 140°/0.2 mm., whence β -chlorocinnamethylamide, m.p. 109°. Treatment of (I) with a suspension of CrCl_2 in $\text{Et}_2\text{O}\cdot\text{HCl}$ gives $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ (II) and β -chlorocinnamaldehyde, b.p. 125°/10 mm. (semicarbazone, m.p. 216°), whilst (II) is produced exclusively when an excess of CrCl_2 is used. α -Bromo- Δ^6 -hexenoic acid, b.p. 134°/12 mm. (ozonised to $\text{Pr}\cdot\text{CHO}$), and SOCl_2 give the corresponding chloride, b.p. 94°/14 mm., whence α -bromo- Δ^6 -

hexenanilide, m.p. 67°. This is converted by successive use of PCl_5 in C_6H_6 and much CrCl_2 into Δ^6 -hexenaldehyde, whilst with a smaller proportion of CrCl_2 the crude α -Br-aldehyde is obtained. Reduction of a halogen atom vicinal to the ethylenic linking appears to depend on the presence of $\cdot\text{CCl}\cdot\text{NR}$ since $\text{CPhCl}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHPh}$, $\text{CPhCl}\cdot\text{CH}_2$, and 1-chloroindene are resistant to CrCl_2 .

H. W.

Formation of hydrocarbons by the thermal decomposition of α -ethoxy-acids. M. MEYER (Compt. rend., 1937, 204, 1260—1261; cf. A., 1933, 377).— β -2-Tetrahydronaphthyl- α -ethoxypropionic acid, b.p. 165°/2 mm. (amide, m.p. 105°; chloride, b.p. 138°/3 mm.), when heated in presence of Pd affords 2-tetrahydronaphthylacetaldehyde, b.p. 161—162°/22 mm. (semicarbazone, m.p. 199—200°), and tetrahydro-2-methylnaphthalene, dehydrogenated (S) to give 2- $\text{C}_{10}\text{H}_7\cdot\text{Me}$. Similarly, β -cinnamyl- α -ethoxypropionic acid gives propenylbenzene.

J. L. D.

Influence of replacement of a β -hydrogen by methyl in α -hydroxy- γ -phenyl- Δ^6 -butenoic acid. M. GIRARD (Compt. rend., 1937, 204, 1071—1073).—Unlike the β -unsubstituted acid (I), α -hydroxy- γ -phenyl- β -methyl- Δ^6 -butenoic acid, m.p. 132° (prep. through its amide, m.p. 161°, and nitrile from $\text{CHPh}\cdot\text{CMe}\cdot\text{CHO}$), is unchanged by heating with alkali, does not react with $\text{I}\cdot\text{Na}_2\text{CO}_3$, affords $\text{CMe}\cdot\text{CHPh}\cdot\text{CH}=\text{CO}$ with strong mineral acids (traces only with weak acids), but like (I) with $\text{I}\cdot\text{NaHCO}_3$ it affords the γ -lactone, m.p. 80°, of β -iodo- $\alpha\gamma$ -dihydroxy- γ -phenyl- β -methylbutyric acid.

J. W. B.

Isomerism of derivatives of cyclohexane. R. D. DESAI, R. F. HUNTER, and G. S. SAHARIA (Nature, 1937, 139, 718—719).—Both 3- and 4-methylcyclohexane-1-carboxylic-1-succinic acids have been isolated in two forms. There is no indication of isomerism with multipanar forms.

L. S. T.

Lichen substances. LXXIX. Components of Cetraria islandica (L.), Ach. II. Y. ASAHINA and M. YASUE (Ber., 1937, 70, [B], 1053—1059).—Examination of new samples of *C. islandica* from Hokkaido gives in some instances solely *d*-protolichesteric acid (I) whereas from others 1-alloprotolichesteric acid (II), m.p. 107°, $[\alpha]_D^{25}$ —102.0° in CHCl_3 , is obtained. The data recorded previously (A., 1936, 314) must be corr. for (II) and its derivatives (pyrazoline compound, $\text{C}_{21}\text{H}_{38}\text{O}_4\text{N}_2$, m.p. 67°, $[\alpha]_D^{25}$ —186.24° in CHCl_3 ; dihydroalloprotolichesteric acid, m.p. 121—123° after softening at about 111°, $[\alpha]_D^{25}$ —57.24° in CHCl_3). Examination of Japanese *C. islandica* shows its components to be very heterogeneous whereas *C. islandica f. tenuifolia* from Japan, which invariably gives a positive $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ test, contains fumarprotocetraric acid alone or mixed with notable quantities of *l*-protolichesteric acid. Examination of European *C. islandica* and *crispa* confirms Zopf's opinion that lichesteric acid is not a primary component but is formed from protolichesteric acid during the extraction. Very mild treatment of *C. islandica f. tenuifolia* from Norway gives, however, a little *l*-lichesteric acid (III) and much (II). Specimens from Baden yielded a mixture

of (II) and (III) whereas another from Lausitz contained (I) almost exclusively. H. W.

Amino-acids. X. α -Methylamino-acids. Synthesis of N-methyl-3:4-dihydroxyphenylalanine and related compounds. T. H. GUERRERO and V. DEULOFEU (Ber., 1937, 70, [B], 947—950; cf. this vol., 19).—Creatinine (I) and vanillin (II) when heated at 140° or boiled in piperidine afford 4-hydroxy-3-methoxybenzylidenecreatinine (III), m.p. 273°, whilst 4-acetoxy-3-methoxybenzylidenecreatinine (IV), m.p. 217°, is obtained by acetylation of (III) or when (I) and (II) are heated with NaOAc and Ac₂O at 130°. Reduction of (III) or (IV) by Na-Hg in H₂O gives 4-hydroxy-3-methoxybenzylcreatinine (V), m.p. 231—233°, or 4-hydroxy-3-methoxybenzylacetylcreatinine, m.p. 174°. (V) is hydrolysed by boiling conc. Ba(OH)₂ to α -methylamino- β -4-hydroxy-3-methoxyphenylpropionic acid, m.p. 276—278° or m.p. 265—267° after darkening at 235° when slowly heated, converted by red P and HI (*d* 1.7) in Ac₂O into α -methylamino- β -3:4-dihydroxyphenylpropionic acid, m.p. 298—300° or m.p. 286—287° after darkening at 240—245° when slowly heated. H. W.

Catalytic oxidation of certain aromatic compounds. J. S. SALKIND and V. V. KESAREV (J. Gen. Chem. Russ., 1937, 7, 879—881).—A mixture of the vapour of the substance with air is passed over 9:1 V₂O₅-U₃O₈ on pumice at 400—420°, when 1- or 2-C₁₀H₇Br or β -C₁₀H₇OH yields *o*-C₆H₄(CO₂H)₂ (I) and BzOH, 1-C₁₀H₇NO₂, or α -C₁₀H₇NH₂ gives *o*-C₆H₄(CO)₂NH and (I), C₅H₅N and quinoline give CO₂, H₂O, NH₃, NO, and H·CO₂NH₄, whilst carbazole is not oxidised at 500°. R. T.

(A) Action of hydrogen chloride on solutions in alcohol of substituted phthalamic acids. (B) Reaction of certain amines with alkylarylphthalamic acids. B. A. PORAI-KOSCHITZ (J. Gen. Chem. Russ., 1937, 7, 604—610, 611—620).—(A) *N*-Arylphthalamic acids in EtOH yield the corresponding *N*-arylphthalimides when the solution is saturated with dry HCl. *N*-*o*- and *p*-Tolyl-, α - and β -naphthyl-, *p*-hydroxyphenyl-, and *p*-dimethylaminophenylphthalimide, m.p. 218° (from *p*-dimethylaminophenylphthalamic acid, m.p. 157°), have been prepared by this reaction. Phenylphthalimide is obtained analogously from *N*-phenylphthalamic acid.

(B) The equilibrium $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHR} + \text{NHR}'\text{R}'' \rightleftharpoons o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NRR}'' + \text{NH}_2\text{R}'$, in various org. solvents at room temp., is shown to exist in the cases R = R' = R'' = Ph; R = R' = Ph, R'' = Me; R = R' = *o*-tolyl, R'' = Et; R = R' = α -C₁₀H₇, R'' = Et. R. T.

Di-*n*-heptyl phthalate.—See A., I, 377.

Friedel-Crafts reaction of lactones. I. Synthesis of aromatically substituted acids from δ -chloro- γ -valerolactone. H. BEYER (Ber., 1937, 70, [B], 1101—1113).— δ -Chloro- γ -valerolactone with AlCl₃ and C₆H₆ at 60—80° affords δ -phenylvaleric acid, m.p. 57—59°, $\gamma\delta$ -diphenylvaleric acid (I), b.p. 180—182°/0.1 mm., anthracene-9:10-dibutyric acid (II), m.p. 248—250°/(vac.) after softening at 240°, and some anthraquinone (III). The intermediate

formation of γ -chloro- δ -phenylvaleric acid is postulated. (I) [*Me* ester, b.p. 155—156°/0.1 mm.; *Et* ester, b.p. 165—166°/0.7 mm.; corresponding chloride (IV), not distillable without decomp.; amide, m.p. 70—71° (vac.); anilide, m.p. 112—113°; carbamido-derivative, m.p. 139—140° after softening at 135°] is also obtained from $\gamma\delta$ -dibromovaleric acid, AlCl₃, and C₆H₆ at 60—70°. (IV) is transformed by AlCl₃ in CS₂ into 1-keto-4-benzyl-1:2:3:4-tetrahydronaphthalene, b.p. 165°/0.1 mm. (semicarbazone, m.p. 186—187°). (II) [*Me*₂ ester, m.p. 106—108° after softening at about 100°; *Et*₂ ester, m.p. 103—105° after softening at about 90°; dihydrazide, m.p. 258—259° (decomp.) after softening at 255°], which has an intense violet fluorescence, is hydrogenated (PtO₂ in AcOH at room temp.) to the non-fluorescent 1:2:3:4-tetrahydroanthracene-9:10-dibutyric acid, m.p. 230—232° after softening at 223° [*Me*₂ ester, m.p. 80—82° (decomp.) after softening at 75°; *Et*₂ ester, m.p. 92—93° after softening at 89°; dihydrazide, m.p. 250—252° (decomp.) after softening]. Ozonisation of (II) gives (III) and (·CH₂·CO₂H)₂. Addition of maleic anhydride to (II) at 260° gives the 9:10-adduct, m.p. 283—285° (decomp.) after softening at 280° (*Me*₂ ester, m.p. 187—189° after softening at 170°), which could not be hydrogenated. H. W.

Manufacture of chrysenecarboxylic acids.—See B., 1937, 420.

Synthesis of α -phenylparaconic acids. M. P. GERTSCHUK (J. Gen. Chem. Russ., 1937, 7, 980—982).—Et₂ β -formyl- α -phenylsuccinate is reduced by Al to Et₂ phenylitamate, which when distilled yields a mixture of cryst. (I), m.p. 92°, and liquid Et₂ α -phenylparaconate (II), b.p. 212—213°/15 mm. (I) or (II) gives α -phenylparaconic acid, m.p. 124° (+ 0.25H₂O, m.p. 102°), when hydrolysed with 10% HCl. R. T.

Electrolysis of aromatic acids. IV. Electrolysis of phthalic acid. V. M. RODIONOV, V. M. LEVTSCHENKO, and V. C. ZVORIKINA. **V. Electrolysis of hemipinic acid.** V. M. RODIONOV and V. C. ZVORIKINA (Bull. Soc. chim., 1937, [v], 4, 463—473, 473—477; cf. this vol., 101).—IV. Anodic or cathodic electrolysis does not affect *o*-C₆H₄(CO₂K)₂. Electrolysis without a diaphragm or first anodically and then cathodically gives α , m.p. 268—269°, and β -di-dihydrophthalyl, (CO<C₆H₄>CH)₂, m.p. 252°, phthalide, and a little *o*-CHO·C₆H₄·CO₂H (I) and BzOH. Probably (I) is first produced by way of peroxides, since cathodic reduction thereof gives the other products. BzOH is formed by loss of CO₂ from (I).

V. Electrolysis of K₂ hemipinate gives only small yields of ψ -meconine. R. S. C.

Enolisation of β -ketonic acids and the absence of their ketonic decompositions in accordance with Bredt's rule. J. BREDT (J. pr. Chem., 1937, [ii], 148, 221—224).—Theoretical. The failure of 2:6-diketodiamontane-1:3:5:7-tetracarboxylic acid (this vol., 152) to lose CO₂ agrees with Bredt's rule that a β -ketonic acid is as stable as a γ - or other ketonic acid when it cannot give rise to an unsaturated

enolic form, and with the impossibility of a double linking being formed at a bridge-head. E. W. W.

$\alpha\beta$ -Unsaturated aldehydes. III. The two **cyclocitrylideneacetaldehydes**. J. VON BRAUN and P. KURTZ (Ber., 1937, 70, [B], 1009—1012).—The possibility that cyclisation occurs during the prep. of citrylideneacetaldehyde (I) from citrylideneacetic acid (von Braun and Rudolph, A., 1934, 1335) is excluded by the observation that the properties of (I) differ from those of the cyclic compounds now prepared. (I) and the compound of Kuhn *et al.* (A., 1936, 316) are probably therefore *cis-trans*-isomerides. α -cycloCitral, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}=\text{CMe} \end{smallmatrix}\rangle\text{CH}\cdot\text{CHO}$,

b.p. 75–77°/10 mm., is converted by Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ into *Et* β -hydroxy- β -2:2:6-trimethyl- Δ^4 -cyclohexenylpropionate, b.p. 147–152°/12 mm. The corresponding hydroxy-acid, m.p. 112–114°, is converted by Ac_2O and NaOAc at 100° into α -cyclocitrylideneacetic acid, b.p. 145–150°/0.05 mm., transformed by SOCl_2 into the corresponding chloride and thence by NH_4Ph in Et_2O into α -cyclocitrylideneacetanilide, b.p. 218–222°/0.05 mm. The latter is converted by the successive action of PCl_5 in C_6H_6 and of CrCl_2 in $\text{HCl}\cdot\text{Et}_2\text{O}$ into α -cyclocitrylideneacetaldehyde, b.p. 82.83°/0.1 mm., which resembles tetrahydroionone in odour. Similarly, β -cyclocitral, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}=\text{CMe} \end{smallmatrix}\rangle\text{C}\cdot\text{CHO}$, b.p. 90–92°/10 mm., is transformed into a mixture of hydroxy- and unsaturated ester from which β -cyclocitrylideneacetic acid, b.p. 146–150°/0.05 mm., is isolated. This is transformed into β -cyclocitrylideneacetanilide, b.p. about 220°/0.05 mm., whence somewhat impure β -cyclocitrylideneacetaldehyde which resembles β -ionone in odour. H. W.

Synthesis of benzylidene-ethylideneazaine. S. A. TEBINOV (J. Gen. Chem. Russ., 1937, 7, 654–655).— PhCHO , MeCHO , and aq. N_2H_4 at 100° yield benzylidene-ethylideneazaine, $\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{CHMe}$, m.p. 89–90°, which does not reduce Ag_2O or Fehling's solution. R. T.

Lichen substances. LXXVIII. Psoromic acid. II. Y. ASAHINA and H. HAYASHI [with, in part, M. TASAKA] (Ber., 1937, 70, [B], 810–812; cf. A., 1933, 823).—Treatment of parinic acid with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at 37° yields acetylpsoromic acid, $\text{C}_{20}\text{H}_{16}\text{O}_3$, m.p. 223°, converted by Ac_2O containing conc. H_2SO_4 into psoromic acid triacetate, m.p. 198–199°.

Hypopsoromic acid (*A*, *R* = Me) is transformed by boiling 10% KOH into hypoparrellic acid, m.p. 253° (decomp.), converted by short treatment with CH_2N_2 into the *Me* ester, m.p. 196–

197°, by protracted treatment into the *Me* ester *Me*₂ ether, m.p. 135°, and by Me_2SO_4 into the *Me*₂ ether, m.p. 230°. Successive electrolytic and catalytic reduction of the latter substance leads to deoxyhyposalazinol *Me*₃ ether, thus establishing the structure of psoromic acid (*A*, *R* = CHO) from the analytical side. H. W.

Reactions of cyclohexanone with diazoethane. A. P. GIRATTIS and J. L. BULLOCK (J. Amer. Chem. Soc., 1937, 59, 951).—cycloHexanone (I) and CHMeN_2 in Et_2O or $\text{Et}_2\text{O}\cdot\text{MeOH}$ give 2-methylcycloheptanone, reaction being faster than with CH_2N_2 . CH_2N_2 does not react with cycloheptanone (II), whilst with cyclopentanone it gives a poor yield of (II) with a little (I). 2-Chlorocyclohexanone with CH_2N_2 gives quantitatively a chloromethylcycloheptanone.

R. S. C.

Synthesis of polyterpenoid compounds. III. J. W. COOK and C. A. LAWRENCE (J.C.S., 1937, 817–827; cf. Chuang *et al.*, A., 1936, 988).—*Et* 2- γ -cyanopropylcyclohexanone-2-carboxylate, b.p. 163–165°/0.7 mm., prepared from γ -iodobutyronitrile and *Et* cyclohexanone-2-carboxylate, is hydrolysed to octane- $\alpha\delta$ -tricarboxylic acid, b.p. 280–290°/0.8 mm. (*Et* ester, b.p. 162–163°/1 mm.), and γ -2-ketocyclohexylbutyric acid (*p*-phenylphenacyl ester, m.p. 78–79°; *Et* ester, b.p. 136°/0.4 mm.). γ -(2-Methyl- Δ^1 -cyclohexenyl)butyric acid (*p*-phenylphenacyl ester, m.p. 83–84°), obtained from MgMeI and *Et* γ -2-ketocyclohexylbutyrate, is cyclised to 9-methyl- Δ^4 : 10 or δ : 10 -1-octalone, m.p. 222–223° (decomp.) (2:4-dinitrophenylhydrazine, m.p. 133°), hydrogenated to 9-methyl-1-decalone [oxime, m.p. 108.5–111°; 2:4-dinitrophenylhydrazine, m.p. 159–160° (decomp.)]. *Et* β - Δ^1 -cyclohexenylethylmethylmalonate, b.p. 134–137°/0.5 mm., from β - Δ^1 -cyclohexenylethyl bromide and $\text{CHMe}(\text{CO}_2\text{Et})_2$, is hydrolysed to the acid, m.p. 141.5–142.5°, which when heated affords γ - Δ^1 -cyclohexenyl- α -methylbutyric acid, b.p. 140–145°/0.8 mm. (*p*-phenylphenacyl ester, m.p. 88–90.5°); this is cyclised through the chloride and SnCl_4 to 2-methyl- Δ^9 : 10 -1-octalone, b.p. 129°/13 mm. [semicarbazone, m.p. 212° (decomp.); oxime, m.p. 160–161°; 2:4-dinitrophenylhydrazine, m.p. 219–220° (decomp.)], which is hydrogenated to 2-methyl-1-decalone, b.p. 109°/11 mm. [semicarbazone, m.p. 216–217.5° (decomp.); oxime, m.p. 152–153.5°; 2:4-dinitrophenylhydrazine, m.p. 223–224.5°]. Hydrolysis and decarboxylation of *Et* β -(4-methyl- Δ^1 -cyclohexenyl)propylmalonate gives in small yield γ -(4-methyl- Δ^1 -cyclohexenyl)valeric acid, b.p. 112–114°/0.14 mm., cyclised to 1:6-dimethyl- Δ^9 : 10 -4-octalone, b.p. 141°/13 mm. [oxime, m.p. 98–102°; semicarbazone, m.p. 163–165.5°; 2:4-dinitrophenylhydrazine, m.p. 217.5–219° (decomp.)]. *Et* γ -bromovalerate and *Et* 5-methylcyclohexanone-2-carboxylate form the keto-ester, hydrolysed to γ -(2-keto-4-methylcyclohexyl)valeric acid, b.p. about 160°/0.8 mm. (semicarbazone, m.p. 177–178.5°). γ - Δ^1 -cyclohexenylbutyric acid is converted through the chloride and AlCl_3 into Δ^9 : 10 -1-octalone [2:4-dinitrophenylhydrazine, m.p. 266.5–267° (decomp.)]; the 2:4-dinitrophenylhydrazine of *trans*-1-decalone (I) has m.p. 222–222.5°. β -2-Ketocyclohexylpropionic acid [semicarbazone, m.p. 181–182° (decomp.)] is hydrogenated to the lactone of β -2-hydroxycyclohexylpropionic acid, b.p. 145°/10 mm.

Methylation ($\text{NaNH}_2\cdot\text{MeI}$) of (I) gives chiefly 2-methyl-1-decalone and some 9-Me compound with a methyl-1-decalone, isolated as the oxime, m.p. 139–139.5°. *cis*-2-Decalone (II) is chlorinated to 3-chloro-*cis*-2-decalone, m.p. 107–108°, converted

into the 3-*OH*-compound, m.p. 88–90°. $\text{Et}_2\text{C}_2\text{O}_4$ and (II) afford *Et cis*-2-ketodecalyl-3-glyoxylate (2:4-dinitrophenylhydrazone, decomp. 181–186°), converted into *Et cis*-2-decalone-3-carboxylate, b.p. 130°/0.7 mm. [2:4-dinitrophenylhydrazone, m.p. 169–170.5° (decomp.)]. This ester and MeI form *Et 3-methyl-cis-2-decalone-3-carboxylate*, b.p. 108.5–110°/0.4 mm. (2:4-dinitrophenylhydrazone, m.p. 120–121.5°), dehydrogenated (Se) to 3-methyl-2-naphthol (III). *Et trans*-2-decalone-3-carboxylate [2:4-dinitrophenylhydrazone, m.p. 181.5–182° (decomp.)] is methylated to *Et 3-methyl-trans-2-decalone-3-carboxylate*, b.p. 113°/0.5 mm. (2:4-dinitrophenylhydrazone, m.p. 102.5–104°), dehydrogenated to (III). $\text{CH}_2\text{Ph}\cdot\text{MgCH}_2\text{Cl}$ and (II) give 2- β -phenylethyl-*cis*-2-decalol, m.p. 111–112°, dehydrated (KHSO_4) to 2- β -phenylethyl-*cis*- $\Delta^{2:3}$ -octalin, b.p. 148–149°/0.9 mm., which is cyclised to dodecahydro-1:2-benzanthracene (IV), similarly prepared from *trans*-2-decalone (V). Dehydrogenation of (IV) affords 1:2-benzanthracene [2:7-dinitroanthraquinone complex, m.p. 252–253° (decomp.)], and its 5:6:7:8- H_4 -derivative, octahydro-1:2-benzanthracene, m.p. 124.5–125.5°, and chrysene. Acetyl- Δ^1 -cyclohexene and (V) give 3-keto- Δ^4 -hexadecahydro-1:2-benzanthracene (*trans* form), b.p. 192–195°/1.3 mm. [semicarbazone, m.p. 240.5–241.5° (decomp.)]; 2:4-dinitrophenylhydrazone, m.p. 201.5–204° (decomp.)], and the ketone (*cis* form), m.p. 122–122.5° [semicarbazone, m.p. 258.5° (decomp.)]; 2:4-dinitrophenylhydrazone, m.p. 172.5–179° (decomp.)], is similarly obtained from (II). These results show that the striking differences in the position of substitution in the stereoisomeric sterol ketones do not hold in the case of the 2-decalones, both *cis*- and *trans*- being attacked at position 3. The stability of the alternative Δ^1 - and Δ^2 -octalin systems present in the enolic forms of the ketones is influenced by the locking of this portion of the sterol mol. with the remainder of the ring system.

F. R. S.

Fission of ketones with alkalis. I. Chloroacetophenones. G. LOOK and E. BÖCK (Ber., 1937, 70, [B], 916–925).—Fission of chloroacetophenones with at least one free *ortho* position occurs, if at all, with production of the corresponding benzoic acid; the change is therefore similar to that caused by substitution of halogen in *Me*. If both *ortho* positions are occupied smooth scission to halogenobenzene and AcOH is observed. Di-*o*-substituted acetophenones therefore closely resemble di-*o*-substituted benzaldehydes. The substance is heated with 50% KOH at 150° in a Ni tube for 24 hr., then diluted with H_2O and extracted with Et_2O . The alkaline solution is acidified with H_3PO_4 and distilled with steam; the distillate is titrated with 0.1N- KOH . COPhMe gives a little BzOH whilst *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ is derived from *o*- $\text{C}_6\text{H}_4\text{ClAc}$. *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ is transformed into *m*-chlorophenylmethylcarbinol, b.p. 240–246° (corr.)/748 mm., oxidised by CrO_3 in AcOH to *m*- $\text{C}_6\text{H}_4\text{ClAc}$, which yields *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$. *p*- $\text{C}_6\text{H}_4\text{ClAc}$ affords *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$. 2:6- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CHO}$ with MgMeI in Et_2O yields 2:6-dichlorophenylmethylcarbinol, b.p. 134–136°/13 mm., m.p. 34–35° (benzoate, m.p. 77°), oxidised to 2:6-

dichloroacetophenone, m.p. 44°, which yields AcOH (= 81%); it is little affected by boiling 89% H_3PO_4 . 2:6- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{H}$ appears stable to 50% KOH . 3:5-Dichlorophenylmethylcarbinol, b.p. 136°/12 mm., m.p. 46°, gives 3:5-dichloroacetophenone, b.p. 134–136°/17 mm., m.p. 26° (*oxime*, m.p. 138°), whence 3:5- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{H}$. 2:4-Dichlorophenylmethylcarbinol, b.p. 130–134°/11 mm. (*p*-nitrobenzoate, m.p. 113°), yields 2:4- $\text{C}_6\text{H}_3\text{Cl}_2\text{Ac}$, m.p. 29° (*oxime*, m.p. 148°). 2:3:6-Trichlorophenylmethylcarbinol, b.p. 149–155°/11 mm., m.p. 87–88° (benzoate, m.p. 106.5°), is oxidised to 2:3:6-trichloroacetophenone, m.p. 63°, which gives 1:2:4- $\text{C}_6\text{H}_3\text{Cl}_3$ in 82% yield. The conversion of 2:4:6-trichlorophenylmethylcarbinol, b.p. 158–163° (corr.)/17 mm., m.p. 76.5°, into 2:4:6-trichloroacetophenone, m.p. 51.5°, which gives 1:3:5- $\text{C}_6\text{H}_3\text{Cl}_3$ is described. Pentachloroacetophenone, m.p. 90°, affords C_6HCl_5 and AcOH (77.5%).

H. W.

Polymethylbenzenes. XVI. Enolising action of magnesium methyl iodide upon hindered ketones. L. I. SMITH and C. GUSS (J. Amer. Chem. Soc., 1937, 59, 804–806; cf. A., 1936, 323).—The no. of active H found and mols. of MgMeI added in the Grignard machine (A., 1928, 160) are, respectively, for aceto-phenone 0.025, 1.025, *m*-xylene 0.05, 1.02, mesitylene 1.03, 0, *o*-durene 0.97, 0.04, prehnitene 0.75, 0.27, and pentamethylbenzene, b.p. 144–145°/8 mm., m.p. 84°, 0.93, 0.01, 3:5-diaceto-1.66, 0.44, and 5-aceto-*p*-cumene 0.25, 0.79, 2:4-diaceto-*m*-xylene (I) 0.16, 1.82, diaceto-mesitylene 1.82, 0.26, *o*-durene (II) 1.62, 0.54, and prehnitene (III), m.p. 113°, 1.68, 0.46. The large effect of *Me o*- to the CO is general, but *Me* in other positions also has some effect. The structure of (I) seems doubtful in view of its low result. Some (II) is formed in the prep. of (III) owing to demethylation of prehnitene by AlCl_3 .

R. S. C.

Reactions in the presence of metallic halides.

I. β -Unsaturated ketone formation as a side-reaction in Friedel-Crafts acylations. N. O. CALLOWAY and L. D. GREEN (J. Amer. Chem. Soc., 1937, 59, 809–811).—In the reaction of C_6H_6 , AcCl , and AlCl_3 in CS_2 evolution of HCl never ceases; some dyppone (I) is formed if the $\text{COPhMe}:\text{AlCl}_3$ ratio is $>1:1$. 2 mols. of COPhMe and 1 mol. of AlCl_3 in CS_2 at 40–50° give 73% of (I), which is also obtained with (?) $\text{CPh}_2\cdot\text{CH}_2$ from COPhMe by AlPh_3 . 1 mol. each of COPhMe , PhCHO , and AlCl_3 give 91% of chalcone. Reaction may occur by way of $\text{AlR}_2\cdot\text{OR}$.

R. S. C.

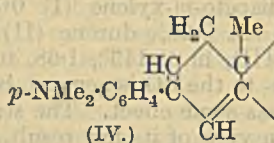
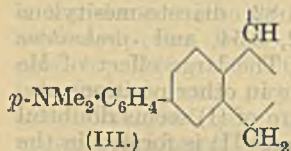
Application of the principle of vinylogy to unsaturated ketones. R. E. CHRIST and R. C. FUSON (J. Amer. Chem. Soc., 1937, 59, 893–897).—The CH_2 in $:\text{CH}_2\cdot\text{C}(\text{OK})\cdot\text{CO}_2\text{Et}$ is reactive, even if the C:C is in a ring and the CO is outside it. Thus, Δ^1 -tetrahydrobenzophenone (prepared from cyclohexene, BzCl , and AlCl_3 in CS_2), b.p. 147°/8 mm., gives (NaOEt) the β -benzylidene derivative, m.p. 115°, and with KOEt and $\text{Et}_2\text{C}_2\text{O}_4$ the oxalo-ester

$\text{COR}\cdot\text{C}=\text{CH}$
 $[\text{CH}_2]_3\cdot\text{C}(\text{OK})\cdot\text{CO}_2\text{Et}$ (I; $\text{R} = \text{Ph}$), m.p. 92° (enolic *K* salt and acetate, m.p. 92°). Δ^1 -Tetrahydroacetophenone (modified prep.) condenses with PhCHO

first at the Me, giving 1-cinnamoyl- Δ^1 -cyclohexene (II), m.p. 68°, which gives no CHI_3 and is also obtained from cyclohexene and CHPh:CH:COCl . (II) and $\text{Et}_2\text{C}_2\text{O}_4$ give the ester (I; $\text{R} = \text{CO:CH:CHPh}$), m.p. 131—132° (K salt). Further treatment of the crude mixture of benzylidenecarvones with PhCHO yields an amorphous substance, probably the dibenzylidene derivative. R. S. C.

Indones. XIV. Partial dehalogenation of the 2:3-dichloro-3-phenyl-2-methylhydrindone of m.p. 111—112°. R. DE FAZI and F. PIRRONE (Gazzetta, 1937, 67, 128—132).—In EtOH this compound (this vol., 153) is converted by AgNO_3 into a compound, $\text{C}_{16}\text{H}_{12}\text{OCl}$ [*sic*] (I), m.p. 125—126°, with an isomeride (II), m.p. 131—132°. With Cu , only (I) is obtained; with KI , a second isomeride (III), m.p. 153—155°, (I), a compound (IV), m.p. 143—144°, and 3-phenyl-2-methylindone (V). In COMe_2 , aq. KOH gives (I) and (V). E. W. W.

Debromination of mono- and di-bromo-cholestanone. E. SCHWENK and B. WHITMAN (J. Amer. Chem. Soc., 1937, 59, 949—950).—Debromination of bromo- (I) and dibromo-cholestanone (II) gives varying results according to the reagent used. With $\text{C}_5\text{H}_5\text{N}$ (I) gives the pyridinium compound, m.p. 125—126°, and (II) gives the pyridinium compound, $\text{C}_{32}\text{H}_{48}\text{ONBr}$, decomp. $>280^\circ$. With NPhMe_2 (I) gives cholestanone and (II) gives a compound, m.p. 230—232°, which couples with



$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ and is (III) or, less probably, (IV). Similarly with KOPh (II) gives a compound, which couples and is probably the hydroxydiphenyl derivative. R. S. C.

Synthetic studies in the sterol and sexual hormone group. I. Synthesis of a 3-keto-10-hydroxyhexahydrochrysene and its methyl ether. C. K. CHUANG, Y. L. TIEN, and Y. T. HUANG (Ber., 1937, 70, [B], 858—863).—Me δ -keto- η -m-methoxyphenyloctoate is cyclised by conc. H_2SO_4 at -15° to Me γ -6-methoxy-3:4-dihydro-1-naphthylbutyrate, b.p. 157—158°/0.3 mm., hydrolysed to the corresponding acid, m.p. 79—80°, which is dehydrogenated by S at 190—200° to γ -6-methoxy-1-naphthylbutyric acid (I), m.p. 150°. (I) is transformed by SOCl_2 in CHCl_3 followed by condensation with $\text{Et}_2\alpha$ -acetylsodioglutarate into the non-cryst. ester $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot[\text{CH}_2]_3\cdot\text{CO}\cdot\text{CAc}(\text{CO}_2\text{Et})\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$, hydrolysed to δ -keto- η -6-methoxy-1-naphthylolcoic acid. The Me ester of this acid is transformed by NaOEt in Et_2O into β -6-methoxy-1-naphthylethylcyclohexane-2:6-dione (II), m.p. 168—170°, which has a pseudo-acidic character but does not give a colour with FeCl_3 . Cyclisation of (II) with P_2O_5 in boiling C_6H_6 or with 80% H_2SO_4 at 100° affords 3-keto-10-methoxychrysene (III), m.p. 177—178°, (oxime, m.p. 263° in bath pre-heated to 250°), which decolorises KMnO_4 in AcOH and gives a red ppt. with Br in CCl_4 . (III)

is demethylated by HBr (d 1.49) in AcOH at 110° to 10-hydroxy-3-ketochrysene, m.p. 257—258° (decomp.) (bath preheated to 245°) [oxime, m.p. 287—288° (decomp.)], converted by 30% KOH and Me_2SO_4 into (III). H. W.

Projected synthesis of testosterone. R. ROBINSON (Chem. and Ind., 1937, 534).—Mainly polemical against Cook (cf. this vol., 292). Methylcyclohexanone probably resembles a cholestanone rather than a β -decalone; a third ring has been added to this hydrindanone. R. S. C.

Condensation of dehydroandrosterone with ethyl α -chloropropionate. W. A. YARNALL and E. S. WALLIS (J. Amer. Chem. Soc., 1937, 59, 951—952).—Dehydroandrosterone, $\text{CHMeCl}\cdot\text{CO}_2\text{Et}$, and NaOEt give the oxide (I) and a little androstene-3:17-diol. NaOH converts (I) into the corresponding acid (Na salt) and a mixture of ketones, probably Δ^5 - and Δ^5 -iso-pregnenolone, formed by rearrangement. R. S. C.

Constitution of artostenone, a ketonic sterol from Artocarpus integrifolia. M. C. NATH (Z. physiol. Chem., 1937, 247, 9—22).—The unsaponifiable portion of the Et_2O extract of the juice of the fruit yields artostenone (I), $\text{C}_{39}\text{H}_{50}\text{O}$, m.p. 109°, $[\alpha]_D^{25} +19.86^\circ$ in abs. EtOH , $+23.44^\circ$ in CHCl_3 [oxime, m.p. 175°; semicarbazone (II), m.p. 203—204° (decomp.)]; Br-derivative, $\text{C}_{39}\text{H}_{48}\text{OBr}_4$, m.p. 160°. (I) with Pt-asbestos and H_2 at 65° gives artostanone (III) (dihydroartostenone), m.p. 106—107° (oxime, m.p. 192—194°), the double linking in the $\alpha\beta$ -position to the keto-group being reduced, and with Na in EtOH or $\text{C}_5\text{H}_{11}\cdot\text{OH}$ artostenol, m.p. 106—107° (acetate, m.p. 120—121°). (II) is only partly reduced by Na in EtOH but the semicarbazone of (III) gives artostane, $\text{C}_{39}\text{H}_{54}$, m.p. 101° [picrate, m.p. 163° (decomp.)]. (I) is not reduced by Zn-Hg . W. McC.

Pechmann's colouring matters. Synthesis of colours with different substituents. P. CHOVIN (Compt. rend., 1937, 204, 1073—1075).—In agreement with earlier results (this vol., 150) it is shown that, in five further cases, the same substance is formed by condensation of either $\text{COAr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}\cdot\text{COAr}'\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ or $\text{COAr}'\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}\cdot\text{COAr}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$, and thus are prepared the compounds of general formula $\text{Ar}(\text{C}_6\text{H}_4\text{O}_4)\text{Ar}'$ where $\text{Ar}, \text{Ar}' = \text{Ph}$, β - C_{10}H_7 , m.p. 297°; Ph , p - $\text{C}_6\text{H}_4\text{Br}$, m.p. 347°; p - $\text{C}_6\text{H}_4\text{Me}$, β - C_{10}H_7 , m.p. 316°; p - $\text{C}_6\text{H}_4\text{Br}$, β - C_{10}H_7 , m.p. 377°; p - $\text{C}_6\text{H}_4\text{Me}$, p - $\text{C}_6\text{H}_4\text{Br}$, m.p. 393°; and p - $\text{C}_6\text{H}_4\text{Br}$, p - $\text{C}_6\text{H}_4\text{Br}$, m.p. 432°. J. W. B.

Kinetics of the sulphuric acid condensation of o-benzoylbenzoic acid. C. W. DEANE (J. Amer. Chem. Soc., 1937, 59, 849—853).—Ring-closure of $\text{o-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$ (modified purification), m.p. 127.2—128.5° (corr.), in 96%—fuming H_2SO_4 (up to 28% SO_3) is unimol., giving 97—99% yields of anthraquinone; it is catalysed positively by SO_3 and negatively by H_2O . Increase of the % SO_3 from 1.8 to 14% has little effect on the rate of ring-closure; this is ascribed

to H_2O formed at $75\text{--}85^\circ$ thus: $\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{H}_2\text{O}$.
R. S. C.

Isomerisation of linalool under the influence of active silicate (floridin). G. V. FIGULEVSKI, E. T. KANETZKAJA, and M. A. PLATONOVA (J. Gen. Chem. Russ., 1937, 7, 873—878).—*d*-Linalool and floridin at $95\text{--}102^\circ$ yield *l*-terpineol, *l*-limonene, dipentene, terpin hydrate, and a dicyclic diterpene, b.p. $178\text{--}180^\circ/6$ mm., with 3 double linkings.

R. T.

Certain transformations of linalool, connected with its stereoisomerism. I. I. VANIN and A. A. TSCHERNOJAROVA (J. Gen. Chem. Russ., 1937, 7, 885—892).—*d*-Linalool in CHCl_3 and PCl_5 yield *l*-linalyl chloride (I) and a dichloride (II) [by addition of HCl to (I)]; with PCl_5 only (I) is formed. (I) is converted by NiCO_3 at $130\text{--}140^\circ$ into a monocyclic terpene, b.p. $62\text{--}72^\circ/6$ mm., and (II) into dihydro-*p*-cymene. (I) gives β -pinene with Ag_2CO_3 , and *l*-linalool with wet Ag_2O , or with KOH in MeOH at 15° .

R. T.

Syntheses with aliphatic monoterpenes. T. WAGNER-JAUREGG and H. ARNOLD (Annalen, 1937, 529, 274—287).—The effects of steric hindrance are very obvious during the production of acids $\text{CHRR}'\text{CO}_2\text{H}$ ($\text{R} = \text{cyclohexyl}$, *cyclopentyl*, or *cyclopentenyl* and $\text{R}' = \text{geranyl}$, *citronellyl*, or *dihydro-citronellyl*) by the malonic synthesis. Introduction of the alkyl residue into $\text{CH}_2(\text{CO}_2\text{Et})_2$ is satisfactorily effected in EtOH at 140° or in boiling xylene. Prolonged hydrolysis of esters $\text{CRR}'(\text{CO}_2\text{Et})_2$ with boiling conc. alkali in many cases gives much *Et H* ester, the complete hydrolysis of which is effected only after decarboxylation. The following are described: *citronellyl chloride*, b.p. $93\text{--}95^\circ/12$ mm., and *bromide*, b.p. $103\text{--}105^\circ/13$ mm.; *geranyl chloride*, b.p. $103^\circ/14$ mm., and *bromide*, b.p. $110\text{--}112^\circ/13$ mm.; *Et*₂ *cyclopentyl*-, b.p. $135\text{--}140^\circ/12$ mm., *cyclopentenyl*-, b.p. $130\text{--}135^\circ/2$ mm., *cyclohexyl*-, b.p. $137\text{--}140^\circ/0.1$ mm., *dihydrocitronellyl*-, b.p. $140\text{--}150^\circ/1$ mm., *citronellyl*-, b.p. $133\text{--}138^\circ/0.2$ mm., and *geranyl*-, b.p. $140\text{--}150^\circ/0.25$ mm., *-malonate*; *Et*₂ *citronellylcyclopentyl*-, b.p. $166\text{--}174^\circ/0.15$ mm., *dihydrocitronellylcyclopentyl*-, b.p. $160\text{--}162^\circ/0.15$ mm., *geranylcyclopentyl*-, b.p. $159\text{--}167^\circ/0.20$ mm., *geranylcyclopentenyl*-, b.p. $160\text{--}167^\circ/2$ mm., *citronellylcyclohexyl*-, b.p. $178\text{--}188^\circ/0.3$ mm., *methylgeranyl*-, b.p. $160\text{--}170^\circ/7$ mm., and *n-hexylcitronellyl*-, b.p. $165\text{--}174^\circ/0.3$ mm., *-malonate*; *geranylcyclopentenyl*-, b.p. $160\text{--}165^\circ/2.5$ mm. (*Et* ester, b.p. $125\text{--}135^\circ/2$ mm.), *geranylcyclopentyl*-, b.p. $170\text{--}190^\circ/0.2$ mm. (*Et* ester, b.p. $154\text{--}165^\circ/3$ mm.); CH_2Ph ester, b.p. $200\text{--}210^\circ/0.4$ mm.; obtained from the acid and $\text{CH}_2\text{Ph}\cdot\text{OH}$ containing Zn dust), *citronellylcyclopentyl*-, b.p. $145\text{--}150^\circ/0.3$ mm. (*Et* ester, b.p. $145\text{--}150^\circ/0.8$ mm.), *citronellylcyclohexyl*-, b.p. $165\text{--}170^\circ/0.4$ mm. (*Et* ester, b.p. $148\text{--}150^\circ/0.5$ mm.); CH_2Ph ester, b.p. $211\text{--}216^\circ/0.6$ mm.), and *n-hexylcitronellyl-acetic acid*, b.p. $170\text{--}180^\circ/0.4$ mm. (*Et* ester, b.p. $168\text{--}172^\circ/2$ mm.); CH_2Ph *dihydrocitronellylcyclopentyl*-, b.p. $172\text{--}190^\circ/0.8$ mm., *n-nonylcyclohexyl*-, b.p. $190\text{--}200^\circ/0.5$ mm., and *n-octylcyclohexylethyl*-, b.p. $203\text{--}206^\circ/0.3$ mm., *-acetate*. Citronellal (I) and Mg *cyclohexyl* bromide in Et_2O yield $\beta\gamma$ -*dimethyl-6-cyclohexyl-4 Δ^8 -octen-0-ol* (*cyclohexyl-*

citronellol), b.p. $137\text{--}140^\circ/0.4$ mm. *l-Citronellylcyclohexan-1-ol*, b.p. $130\text{--}140^\circ/0.5$ mm., is derived from Mg *citronellyl* bromide and *cyclohexanone* (II) in Et_2O . Addition of 35% NaOH to (I) and (II) in EtOH at -10° affords *citronellidenecyclohexanone*, b.p. $127\text{--}135^\circ/0.3$ mm. *Methylgeranylbarbituric acid*, m.p. $166\text{--}167^\circ$ (corr.) after softening at 158° , and its H_4 -derivative, m.p. 221° (corr.), are devoid of soporific action.
H. W.

Secondary alcohols from cineole. A. GANDINI (Gazzetta, 1937, 67, 113—119).—2-Ketocineole is reduced by $\text{Na}\text{--}\text{EtOH}$ to a 2-*hydroxycineole*, m.p. $106\text{--}108^\circ$ (*phenylurethane*, m.p. $86\text{--}86.5^\circ$), with a smaller quantity of an *isomeric*, m.p. 80° (*phenylurethane*, m.p. 145°), which is the main product when $\text{Pt}\text{--}\text{H}_2$ is used (cf. Vavon, A., 1926, 837).
E. W. W.

Comparison of methods of bromination of terpenes. T. K. GAPONENKOV (J. Gen. Chem. Russ., 1937, 7, 994—995).—The highest yields of limonene tetrabromide are obtained by Godlewski's method (cf. A., 1899, i, 920).
R. T.

Irreversible catalysis of dicyclic hydrocarbons. Contact transformation of carane. R. J. LEVINA (Sci. Rep. Moscow State Univ., 1934, No. 3, 187—192).—Carane is converted into cymene and menthane by passing over $\text{Pd}\text{--asbestos}$ at $160\text{--}180^\circ$ in a stream of CO_2 . α -Fenchene and 1 : 3 : 3-trimethyl-4-*cyclohexene* are not affected by similar treatment.

R. T.

Preparation of camphorone and of two stereoisomeric dihydrocamphorols. R. CALAS (Compt. rend., 1937, 204, 984—986).—The *d*-camphorone when heated in vac. at 450° affords *dl*-2-methylcyclopentanone (5%), pulegone (17%), and *dl*-camphorone (I) (65%). With Na in $\text{Et}_2\text{O}\text{--}\text{H}_2\text{O}$ (I) gives a mixture, b.p. $82\text{--}84^\circ/15$ mm., of two alcohols, b.p. $83.2^\circ/18$ mm. and $83.3^\circ/18$ mm., which with $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ afford *phthalates*, m.p. 114° (I) and 84° (II), respectively. Hydrolysis of the esters affords the alcohols, which with CrO_3 give dihydrocamphorone (cf. A., 1913, i, 348), indicating that the alcohols are saturated stereoisomerides. The *cis* form (I) is hydrolysed more slowly than the *trans* (II).
J. L. D.

Stereoisomerism of isocamphanol (camphenilyl alcohol) and of ω -aminoisocamphane. W. HÜCKEL and K. HARTMANN (Ber., 1937, 70, [B], 959—963).—Oxidation of *dl*-camphene with $\text{Pb}(\text{OAc})_4$ at 80° gives the *enol acetate* of *camphenilanaldehyde* (I), b.p. $111\text{--}113^\circ/10$ mm., and, apparently, a saturated *isomeride*, m.p. 101° . When warmed with $\text{KOH}\text{--}\text{EtOH}$ (I) gives *camphenilanaldehyde* (II) (semicarbazone, m.p. 223°), also obtained mixed with some *isocamphenylanic acid*, m.p. 118° , but no *camphenilone* when (II) is ozonised in AcOH or moist C_6H_6 . Reduction of (II) by Na and abs. EtOH affords preponderatingly *isocamphanol* I (III), m.p. 84° (*p-nitrobenzoate*, m.p. 109° ; *H phthalate*, m.p. 139°). Hydrogenation ($\text{Pt}\text{--sponge}$ in Et_2O) of (I) or (II) gives mainly *isocamphanol* II (IV), m.p. 101° (*p-nitrobenzoate*, m.p. 96° ; *p-aminobenzoate*, m.p. 131° ; *H phthalate*, m.p. 144°). The rates of hydrolysis of the esters of (III) and (IV) differ very greatly from one another. NH_2OH , HCl and (II) give a non-cryst.

oxime, reduced by Na and EtOH to ω -aminocamphane, which gives two Bz derivatives, m.p. 109° and m.p. 130.5°, respectively.

H. W.

Addition of alcohols to double linkings. II. Ethers from unsaturated cyclic hydrocarbons and from the two pinenes. W. TREIBS (Ber., 1937, 70, [B], 589—594; cf. this vol. 157).—*cyclo*-Hexene is unaffected by prolonged action of boiling MeOH containing H₂SO₄ whereas 1-methyl- Δ^1 -*cyclo*-hexene gives 1-methoxy-1-methylcyclohexane, b.p. 149—150°, in >50% yield. 1-Methoxy-1-ethylcyclohexane, b.p. 165—167°, is derived similarly but in poorer yield from 1-ethyl- Δ -cyclohexene. Menthene, obtained by the action of hot H₂C₂O₄ on menthol, affords tert.-menthyl Me ether, b.p. 200—201°. Addition of MeOH occurs to hydrocarbons containing a sec.-tert. but not to those with a sec.-sec. double linking. Homomenthene with a tert.-tert. double linking remains unchanged. Conditions are less favourable and more complicated with cyclic hydrocarbons containing two double linkings, owing to the tendency to the formation of a conjugated system and subsequent polymerisation. Carvene gives small amounts of an ether with 2 OMe, but is mainly dimerised. α -Phellandrene is completely dimerised, whilst the 5-ring hydrocarbon from piperitone oxide is rapidly converted into a mixture of polymerides. Gradual addition of α - or β -pinene to boiling H₂SO₄-MeOH (sulphonic acids, PCl₃, PCl₅, and certain anhyd. salts also accelerate addition) affords α -terpineol Me ether, b.p. 212°, which readily loses MeOH under the influence of hot, conc. HCO₂H, AcOH-H₂SO₄, or various anhyd. salts giving a doubly unsaturated, very unstable hydrocarbon, C₁₀H₁₆, b.p. 182—184°, apparently identical with that derived from α -terpineol.

H. W.

Syntheses in the pinane group. II. Attempted synthesis of pinocamphone and synthesis of trans-s-homopinic acid. P. C. GUHA, K. GANAPATHI, V. K. SUBRAMANIAN, and D. K. SANKARAN (Ber., 1937, 70, [B], 736—742; cf. A., 1936, 855).—Ketonopinone could not be reduced to nopinone or nopinane by Zn dust and AcOH or HCl or by Clemmensen's method. Reduction of *cis*- or *trans*-Et₂ norpinate by Na and EtOH gives trans-1:1-dimethyl-2:4-dihydroxymethylcyclobutane (I), b.p. 152—155°/15 mm. (yield 70—80%), oxidised by KMnO₄ in alkaline solution to trans-norpinic acid. (I) and PBr₃ in anhyd. CHCl₃ give trans-1:1-dimethyl-2:4-dibromomethylcyclobutane, b.p. 100—102°/4 mm., re-converted into (I) by aq. Ba(OH)₂ and transformed by NaCN in EtOH-H₂O into trans-1:1-dimethyl-2:4-dicyanomethylcyclobutane (II), b.p. 142—145°/6 mm. Hydrolysis of (II) by 20% KOH yields trans-2:2-dimethylcyclobutane-1:3-diacetic acid (trans-s-homopinic acid) (III), m.p. 120—121° [anilide, m.p. 216—217°; Et₂ ester (IV), b.p. 131—132°/4 mm.], converted by hot Ac₂O or by Ac₂O at 200° into the mixed anhydride, OAc·CO·CH₂·CH< $\begin{smallmatrix} \text{CMe}_2 \\ \text{CH} \end{smallmatrix}$ >·CH₂·CO·OAc, which can be distilled unchanged, does not give an anilic acid or react with NH₂·CO·NH₂, and is converted by warm H₂O into (III). Distillation of (III) over Ba(OH)₂ does not appear to yield a ketone. The Dieckmann condensation of (IV) does not occur with

Na in boiling C₆H₆, whereas in boiling xylene traces of a product are obtained which gives a brownish-red colour with FeCl₃ and yields a Cu derivative.

H. W.

Syntheses in the thujane group. III. Synthesis of thujane. P. C. GUHA and B. NATH (Ber., 1937, 70, [B], 931—936; cf. A., 1936, 848, 850).—Gradual addition of Br to *l*-menthone in CHCl₃ in absence of light gives 2:4-dibromomenthone, m.p. 78—79°, [α]_D²⁰ +199.2° in CHCl₃, in almost quant. yield. It is debrominated by Zn dust in EtOH to methylisopropylidicyclohexanone (I), b.p. 205—208°/688 mm., [α]_D²⁰ +25.13° (semicarbazones, m.p. 175—176°, [α]_D²⁰ -52.5° in AcOH, and m.p. 150—151°, [α]_D²⁰ -53.0° in AcOH, respectively), and 1-methyl-4-isopropyl- $\Delta^{1:4}$ -cyclohexadien-3-one (II), b.p. 123—125°/14 mm., [α]_D \pm 0°. When heated or treated with HCl (II) passes into thymol. Reduction of (I) by Na and abs. EtOH gives menthol, whereas with Zn-Hg and HCl thujane, b.p. 156—157°, [α]_D²⁰ +8.48°, and *p*-menthane are produced. Treatment of (I) with N₂H₄, HCl and KOAc in dil. MeOH affords the ketazine (N:C₁₀H₁₆)₂, b.p. 175—177°/4 mm., m.p. 78—79°, [α]_D²⁴ +102.5° in Et₂O, whereas the hydrazone, b.p. 123—125°/7—8 mm., [α]_D +2.38° (CHPh derivative, b.p. 162—165°/3—4 mm., [α]_D²³ -21.6° in EtOH), is obtained from (I) and boiling 50% N₂H₄·H₂O.

H. W.

Diene value of essential oils. H. P. KAUFMANN, J. BALTES, and F. JOSEPHS (Ber., 1937, 70, [B], 908—911).—The iodometric method of determining the diene val. is applied to phellandrene and myrcene, the additive products of which with maleic anhydride (I) are indifferent towards I. The compounds from ocimene and α -terpinene behave analogously. The use of the method with various essential oils containing these compounds shows that a sharp endpoint of addition of (I) is reached with comparative rapidity.

H. W.

Lucanöl, a definite principle extracted from the seeds of *Lucerna glauca*, Benth. M. MASORÉ (Compt. rend., 1937, 204, 890—891).—The seeds when extracted with H₂O give the substance *lucanöl*, (C₄H₅O₂N)_x, m.p. about 283—287° (decomp.), responsible for the coloration with FeCl₃. The mol. appears to contain phenolic, NH₂, and possibly CO₂H groups. The coloration with FeCl₃ is violet-blue in acid, deep red in alkaline solution.

F. A. A.

Lignin and related compounds. XXVII. Methylation and structure of methanol-lignin (spruce). J. COMPTON and H. HIBBERT (Canad. J. Res., 1937, 15, B, 38—45; cf. A., 1936, 995).—Crude methanol-lignin (I) (OMe 23%) is composed of two fractions, (i) (OMe 24%) removed by long extraction with Et₂O, or by its insolubility in 8—10% NaOH, and (ii) (OMe 21.6%), sol. in 8—10% NaOH and reprecipitated by cold 1% HCl. (I) with Me₂SO₄ and a slight excess of 7.5*N*-NaOH at 20—40° gives methylated lignins A and B (OMe 32.2 and 35.4%, respectively) (not acetylated by Ac₂O-C₅H₅N), whilst with a large excess of NaOH at 60°

a product (OMe 37.2%) is obtained. Thus new OH groups are formed during methylation (probably from heterocyclic non-furan rings). Such degradation is markedly increased by rise of temp. and by increasing [NaOH], but is restricted by use of COMe₂ as solvent and by use of >5% excess of NaOH at 20°. When refluxed with 65% aq. MeOH-9% H₂SO₄, the OMe content (22.3%) of Et₂O-insol. (I) is reduced to 21.3% in 48 hr. and to 20.9% in 100 hr.

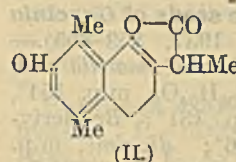
J. W. B.

Lignin. V. Preparation and sulphonation of the lignin from rye straw and pine wood. H. FRIESE [in part with H. GLASSNER] (Ber., 1937, 70, [B], 1059—1071).—Treatment of rye straw with Ac₂O-AcOH (2.5:1) containing 6 vol.-% of H₂SO₄ give α-cellobiose acetate and an undefined mixture of sugar acetates corresponding with the presence of about 75% of carbohydrates. Treatment of the portion of the product sol. in H₂O with MeOH of varied concn. and ultrafiltration of the aq. solutions establishes the formation of ligninsulphonic acids. Similar treatment of pine meal indicates the presence of 65% of carbohydrates, a larger proportion of non-ultrafilterable matter, and a sol. portion similar to that derived from straw. Lignin obtained by use of superconc. HCl or 66% H₂SO₄ which does not contain carbohydrates is not dissolved by Ac₂O-AcOH-H₂SO₄. It appears therefore that a portion of the lignin at any rate is combined with polymeric carbohydrates in wood, but there is no reason to doubt the existence of lignin as such. The incomplete degradation of fir wood is described. H. W.

Lignin. VI. Sulphite liquors. H. FRIESE, V. HÖGN, and H. WILLE (Ber., 1937, 70, [B], 1072—1079).—The liquor is centrifuged and subjected to a short after-hydrolysis with 2—6 vol.-% H₂SO₄ at 100°. After removal of volatile acids the solution is neutralised with CaCO₃ and evaporated to dryness. The residue is divided into three fractions by treatment with boiling MeOH, 80% MeOH, and finally by ultrafiltration. These are acetylated. It is thus established that the contents of the liquor are (i) a complex, non-hydrolysable ligninsulphonic acid, possibly a mixture of isomerides of differing mol. size which can be separated by ultrafiltration, (ii) a mixture of free sugar derivatives largely derived from hemicelluloses, and (iii) lignin-carbohydrate compounds in which the lignin is sulphonated in varying degrees. Treatment of wood with Ca(HSO₃)₂ is regarded as causing sulphonation of the free lignin component, whereby it is rendered at least colloiddally sol. in alkali; the combined lignin is also sulphonated and rendered sol. in H₂O. The acidity of the liquor is not sufficient to cause hydrolysis of the complex. The so-called hemicelluloses, in so far as they are not combined with lignin, are hydrolysed to small components. H. W.

α-Hydroxysantonin. Y. ASAHINA and T. MOMOSE (Ber., 1937, 70, [B], 812—819).—α-Hydroxysantonin (I), m.p. 286°, obtained from the urine of dogs to which santonin has been administered, is converted by boiling Ac₂O containing NaOAc into the acetate, m.p. 173°, from which it is regenerated by cold fuming HCl. It is not esterified when heated

with AcOH at 155° for 1 hr. (I) can be sublimed unchanged in a high vac., but loses H₂O when heated with HCl or HCO₂H, giving the lactone (II), m.p. 244—246°, [α]_D²⁰ +0° in EtOH, (Me ether, m.p. 165—166°; acetate, m.p. 183°). (II) is transformed by 10% NaOH into α-1-keto-7-hydroxy-5:8-dimethyl-1:2:3:4-tetrahydro-2-naphthylpropionic acid, m.p. 192—193° (Me ester, m.p. 138°), which is reduced (Na-Hg) to r-desmotroposantonin, m.p. 198—200° (acetate, m.p. 145°). (II) is reduced (Pd-C in AcOH) to r-santonigenic acid, m.p. 179—180° (Me ester, m.p. 98°), which is oxidised by FeCl₃ in 40% AcOH to disantonigenic acid, C₃₀H₃₈O₆, m.p. 265° (decomp.). (I) is converted by boiling 10% NaOH into the diketone, C₂₂H₁₆O₂, m.p. 106—107°, [α]_D²⁵ -108.9° in EtOH [dioxime, m.p. 244—245° (decomp.); monosemicarbazone, m.p. 240° (decomp.); enol acetate, b.p. 134—135°/3 mm.], which could not be hydrogenated in AcOH or EtOH and remains unchanged when heated with fuming HCl at 100° or with H₂SO₄ (d 1.5). Oxidation by KMnO₄ at room temp. transforms the diketone into the acid, C₇H₁₁(CO₂H)₃, m.p. 164—165°.



(II)

H. W.

Manila elemi resin. M. MLADENOVIC (Monatsh., 1937, 70, 276—280).—Elemi resin should properly be assigned to the resinol class since it is mainly composed of the alcohols, amyrin (I) and brein (II). Treatment of the resin by the customary methods yields an ethereal oil, (I), and elemic acid. The amorphous β-elemic acid of Tschirch is a mixture of various elemic acids and, after acetylation, gives Ac derivatives of the acids with α- (III) and β-amyrin (IV) acetate. Keeping a solution of the residue in EtOH for months results in the separation mainly of (I) and repeated slow evaporation of the mother-liquors gives a cryst. mixture of (I) and (II). Acetylation (Ac₂O-C₅H₅N) of the non-cryst. residue gives (III), (IV), and brein acetate, whilst the remainder appears to contain OH. The Ac val [calc. on (I)] indicates that (I) is present to the extent of about 70%. H. W.

Quassin. I. Preparation and purification of quassin and neoquassin; their molecular formulæ. E. P. CLARK (J. Amer. Chem. Soc., 1937, 59, 927—931).—Treatment of a hot-H₂O extract of quassia chips first with Pb(OAc)₂ and then with activated C, followed by percolation of the C with CHCl₃, gives 0.15—0.18% of a mixture, separated by crystallisation, of quassin (I), C₂₀H₂₄O₄(OMe)₂, m.p. 205—206°, [α]_D²⁰ +40° in CHCl₃, and an isomeride, neoquassin, m.p. 225—226°, [α]_D²⁰ +46.6° in CHCl₃. With 3.5% HCl (I) gives semidemethoxyquassin, C₂₀H₂₅O₅·OMe, m.p. 213°, sol. in aq. NaOH, but insol. in Na₂CO₃ or NaHCO₃, with constant-boiling HCl or HBr gives quassinol, C₂₀H₂₄O₄(OH)₂, m.p. 263° (decomp.), [α]_D²⁵ +62.6° in CHCl₃ [Ac derivative, m.p. 236° (decomp.)], sol. in alkalis, with Ac₂O-NaOAc gives anhydroquassin, C₂₂H₂₈O₅, m.p. 196°, dehydroquassin, C₂₂H₂₈O₆, m.p. 254°, and picrosmin, and with CrO₃ yields an isomeride, m.p. 221°, [α]_D²⁰ +35.1° in CHCl₃, which yields twice as much quassinol as does (I). Crystallo-optical data are recorded. R. S. C.

Reactions caused by "activated" alumina.—See A., I, 368.

Morellin, a constituent of the seeds of *Garcinia morella*. B. S. RAO (J.C.S., 1937, 853-855).—Extraction of the pericarp of seeds of *G. morella* with hot EtOH yields **morellin** (I), $C_{30}H_{34}O_6$, m.p. 154°, $[\alpha]_D^{25}$ -594° (dihydrochloride, m.p. 131°; Br_4 -derivative, m.p. 138-139°, $[\alpha]_D^{25}$ -156°; dioxime, m.p. 148-149°; mononitroguanylhdyrazone, m.p. 205-5°, $[\alpha]_D^{25}$ -748°; tetra-acetate, m.p. 178-179°, $[\alpha]_D^{25}$ -327°; Me_2 ether, m.p. 156°, $[\alpha]_D^{25}$ -242°, and its dioxime, m.p. 118°, $[\alpha]_D^{25}$ +241°, diacetate, m.p. 82-83°, and Br_4 -derivative, m.p. 124°; Me_2 ether, m.p. 170-172°). (I) resinifies on prolonged boiling with EtOH or on keeping at 100° for several hr. and it is converted into an amorphous substance when dissolved in EtOH-KOH. A cryst. isomeride, **isomorellin**, m.p. 116°, $[\alpha]_D^{25}$ -561°, is obtained when an Et_2O solution of (I) is shaken with aq. KOH or when it is digested with $AcCl$ in C_6H_6 solution in the presence of K_2CO_3 . When fused with KOH, (I) gives *dl*-methylheptenol, phloroglucinol, $AcOH$, *isovaleric*, methylsuccinic, and homophthalic acids, and a *ditert*-glycol, $C_{16}H_{22}O_2$, b.p. 130-140°/8 mm. (I) is probably related to mangostin from the pericarp of seeds of *G. mangostana*. P. W. C.

Chinese Asarum, *Asarum Blumei*, Duch, "Hsi-Hsin." Constitution of a neutral component. HUANG-MINLON (Ber., 1937, 70, [B], 951-958).—Extraction of the drug, which is free from alkaloids, with hot light petroleum affords *l*-asarinin (I), m.p. 121-122°, $[\alpha]_D^{25}$ -122° in $CHCl_3$, identical with the product obtained from Korean *Asarum* (cf. A., 1935, 1433). (I) does not decolorise Br in $CHCl_3$ or $KMnO_4$ but gives an orange-yellow colour with $C(NO_2)_4$. It cannot be acetylated and does not give ketonic reactions. OH and OMe are absent. It is unchanged by boiling conc. KOH . Treatment of (I) with conc. HNO_3 in $AcOH$ at room temp. gives *dinitro-l*-asarinin, m.p. 220-221°, $[\alpha]_D^{25}$ +32° in $CHCl_3$, and 4-nitro-1:2-methylenedioxybenzene. Prolonged treatment of (I) with boiling 10% $HCl-EtOH$ causes isomerisation to *l*-sesamin, m.p. 121-122°, $[\alpha]_D^{25}$ -68.9° in $CHCl_3$, and produces small amounts of substances, m.p. 121-122°, 168-169°, and 184-185°, respectively. Similarly *d*-sesamin is isomerised to *d*-asarinin, m.p. 121-122°. *dl*-Sesamin, m.p. 126-127°, and *dl*-asarinin, m.p. 134-135°, are obtained by admixture of the requisite optical antipodes. Attempts to convert (I) into a $(OMe)_4$ -compound are described. The constitution of (I) is discussed.

H. W.

Hydrogenation of alcohols derived from furan. R. PAUL (Bull. Soc. chim., 1937, [v], 4, 846-854).—Furylalkylcarbinols (I) are obtained in good yield by the action of a considerable excess of the requisite Grignard reagent on furfuraldehyde at -15°. The product is decomposed by H_2O and extracted with Et_2O ; the ethereal solution is vigorously shaken with conc. $NaHSO_3$ and then kept over K_2CO_3 to which a little NH_2Ph is finally added. The product is finally distilled under suitable low pressure. Hydrogenation of (I) in presence of Pt or Pd is accompanied by rupture of the nucleus at room temp.; with Ni this

effect becomes more marked as the temp. of reaction is increased. With Raney Ni at 60-80°/50 atm., scission is entirely absent and the change is rapid; the small amount of unchanged (I) is removed, previous to distillation, by treatment of the product with Br in $CHCl_3$ at low temp. or with HCl (1:1). The following compounds are thus obtained: 2-tetrahydrofurylmethylcarbinol, b.p. 71°/16 mm. (phenylurethane, m.p. 83-84°; acetate, b.p. 84°/14 mm.); 2-tetrahydrofuryl ethylcarbinol, b.p. 82-84°/15 mm. (phenylurethane, b.p. about 200-202°/8 mm.; acetate, b.p. 90-91°/12 mm.); tetrahydrofuryl-*n*-propylcarbinol, b.p. 94-95°/14 mm. (phenylurethane, m.p. 75°); phenyl-2-tetrahydrofurylcarbinol, b.p. 147-148°/10 mm. (phenylurethane, m.p. 123-124°; acetate, b.p. 161-163°/11.5 mm.). H. W.

"Furanic" condensations. VII. Preparation of alcohols of the furan series by means of ethereal or individual organomagnesium compounds and their transformation into unsaturated substances and resins. V. V. TSCHELINCEV [with A. S. LARIONOV] (Bull. Soc. chim., 1937, [v], 4, 819-824; cf. A., 1936, 996).—Furfuraldehyde is transformed by $MgEtI$ in Et_2O or, preferably, by $MgEtI$ in $C_6H_6-NPhMe_2$ into 2-furyl ethylcarbinol (I), b.p. 181-183°; 2-furyl isopropylcarbinol (II), b.p. 202-204°/760 mm., is obtained similarly. (I) or (II) is dehydrated by MgI_2 or anhyd. $H_2C_2O_4$ to the corresponding alkylidene compound, which immediately passes into a hard, non-fusible plastic resin. H. W.

Interaction of mixed organomagnesium compounds with ethyl β -furylacrylate. N MAXIM and (MLEE.) E. GEORGESCU (Bull. Soc. chim., 1936, [v], 3, 2266-2270).— $Et \beta$ -2-furylacrylate (I) with $MgEtBr-Et_2O$ yields γ -hydroxy- α -2-furyl- γ -ethyl- Δ^a -pentene, b.p. 125°/16 mm. (*Bz* derivative, b.p. 193°/11 mm.). Similarly (I) with $MgPrBr-Et_2O$ yields γ -hydroxy- α -2-furyl- γ -propyl- Δ^a -hexene, b.p. 130°/16 mm. (*Bz* derivative, b.p. 198°/12 mm.), with $MgBu^tCl-Et_2O$ yields γ -hydroxy- α -2-furyl- ϵ -methyl- γ -isobutyl- Δ^a -hexene, b.p. 143°/17 mm. (*Bz* derivative, b.p. 210°/18 mm.), with *iso*- C_5H_{11} - $MgBr$ yields γ -hydroxy- α -2-furyl- ζ -methyl- γ -isoamyl- Δ^a -heptene, b.p. 174°/12 mm. (*Bz* derivative, b.p. 224°/8 mm.), and with $MgPhBr$ yields γ -hydroxy- α -2-furyl- $\gamma\gamma$ -diphenyl- Δ^a -propene, m.p. 59°. Hydrolysis by $KOH-H_2O$ of all the *Bz* derivatives gives the parent alcohols. Contrary to Thiele's hypothesis the organo-Mg compounds have reacted with the ester group and not with the conjugated system $\cdot CH:CH \cdot CO \cdot$. H. G. M.

Accelerators of vulcanisation.—See B., 1937, 592.

Synthesis of furfurylidene-ethylideneazaine. S. A. TEBINOV (J. Gen. Chem. Russ., 1937, 7, 656-657).—Furfuraldehyde, $MeCHO$, and aq. N_2H_4 at 100° yield furfurylidene-ethylideneazaine, m.p. 109°.

R. T.

Oxidation of acetylene- γ -glycols. 3:4-Diketo-2:2:5:5-tetraphenyltetrahydrofuran. P. A. TICHOMOLOV and A. E. DRUSHININ (J. Gen. Chem. Russ., 1937, 7, 869-872).— $(OH \cdot CPh_2 \cdot C)_2$ in $AcOH$ and CrO_3 yield 3:4 diketo-2:2:5:5-tetraphenyltetrahydrofuran [phenylhydrazone, m.p. 134°; mon-

oxime, m.p. 216° (decomp.); compound with $\text{C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 249—250°]. R. T.

Natural coumarins. XXVII. Fraxidin and isofraxidin. E. SPATH and Z. JERZMANOWSKA-SIENKIEWICZOWA (Ber., 1937, 70, [B], 1019—1020).—The mother-liquors left after isolation of fraxinol (this vol., 254) contain *fraxidin*, m.p. 196—197° (vac.), identified as 8-hydroxy-6:7-dimethoxycoumarin, and *isofraxidin* (I), m.p. 148—149°. The methylation of (I) to 6:7:8-trimethoxycoumarin and its difference from the known hydroxydimethoxycoumarins of the 6:7:8-series prove it to be 7-hydroxy-6:8-dimethoxycoumarin. H. W.

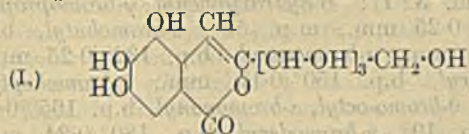
Natural coumarins. XXVIII. Marmelosin. E. SPATH, P. K. BOSE, W. GRÜBER, and N. C. GUHA (Ber., 1937, 70, [B], 1021—1023).—Marmelosin (I), obtained from the fruits of *Aegle marmelos* (Dikshit and Dulb, A., 1932, 1035), is proved by its isomerisation to *alloimperatorin*, the identity of the Me ethers of (I) and *imperatorin* (II), and the characteristic fission with AcOH containing a little H_2SO_4 to be identical with (II). H. W.

Natural coumarins. XXIX. Constitution of osthenol. E. SPATH and J. BRUCK (Ber., 1937, 70, [B], 1023—1024).—Treatment of the residues left from the extracts of *Angelica* root after removal of angelicin and osthol (I) with CH_2N_2 leads to the isolation of further quantities of (I), thus disclosing the presence of *osthenol* [7-hydroxy-8- γ -methyl- Δ^8 -butenylcoumarin], m.p. 124—125°, the direct isolation of which is also described. H. W.

Natural coumarins. E. SPATH (Ber., 1937, 70, [A], 83—117).—A lecture.

Synthetic coumarins. I. Coumarins derived from resacetophenone. R. R. AGARWAL and S. DUTT (J. Indian Chem. Soc., 1937, 14, 109—112).—Condensation of resacetophenone with the appropriate reagent gives 7-hydroxy-6-acetyl-, m.p. 139°, 7-hydroxy-6-acetyl-4-methyl-, m.p. 147° (Ac derivative, m.p. 120—121°; oxime, m.p. 205°; semicarbazone, m.p. 183°; phenylhydrazone, m.p. 146—147°), 7-hydroxy-6-acetyl-3:4-dimethyl-, m.p. 168°, 7-hydroxy-6-acetyl-4-methyl-3-ethyl-, m.p. 122°, 7-hydroxy-6-acetyl-4-methyl-3-isopropyl-, m.p. 108°, and 7-hydroxy-6-acetyl-3-benzyl-4-methyl-coumarin, m.p. 176°, and 7-hydroxy-4-methylcoumarin 6-styryl ketone, m.p. 141°. F. R. S.

Norbergenin. A. E. TSCHITSCHIBABIN, A. V. KIRSANOV, and G. A. ARBUSOV (Bull. Soc. chim., 1936, [v], 3, 2343—2347).—Bergenin is demethylated by 48% HBr to *norbergenin* (I), m.p. 276—278° (decomp.), $[\alpha]_{\text{D}}^{20}$ —32.7° in H_2O (Ac_6 derivative,



m.p. 214—218°, $[\alpha]_{\text{D}}^{20}$ —22.8° in C_6H_6), which also exists in an amorphous form and in another cryst. form with $0.5\text{H}_2\text{O}$. With CH_2N_2 (I) gives dimethylnorbergenin, also obtained from bergenin, and on demethylation gives (I). This confirms the assigned

constitution (I). In H_2O or EtOH with FeCl_3 (I) gives a deep blue coloration which turns brick-red with NaOH. Alkaline solutions of (I) become yellow in presence of atm. O_2 but are decolorised again on acidification. H. G. M.

Hydrogen cyanide synthesis of aromatic aldehydes. I. Dibenzfuran-3-aldehyde. L. E. HINKEL, E. E. AYLING, and J. H. BEYNON (J.C.S., 1937, 778—780).—Dibenzfuran-3-aldehyde (I), m.p. 68° (phenylhydrazone, m.p. 162°; NH_2Ph derivative, m.p. 131°; semicarbazone, m.p. 240°; oxime, m.p. 129°), prepared from dibenzfuran, $\text{C}_2\text{H}_2\text{Cl}_4$, HCN, and AlCl_3 , is oxidised (KMnO_4) to the -carboxylic acid and condenses with benzoin to 3-dibenzfuroyl-3-dibenzfurylcarbinol, m.p. 130°. The carbinol is oxidised (HNO_3) to bis-3-dibenzfuryl ketone, m.p. 236—237°, which is transformed (KOH) into bis-3-dibenzfurylglycollic acid, m.p. 248°. With $\text{NaOAc} \cdot \text{Ac}_2\text{O}$ (I) yields β -dibenzfuran-3-acrylic acid, m.p. 239—240° (Me ester, m.p. 130°), with $\text{CH}_2(\text{CO}_2\text{H})_2$ forms dibenzfuryl-3-methylenemalonic acid, m.p. 213° (decomp.), and with NMe_2Ph gives 3-dibenzfuryl-pp'-bis(dimethylamino)diphenylmethane, m.p. 172°, oxidised to an intense green dye. F. R. S.

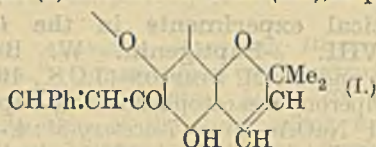
Synthetical experiments in the isoflavone group. VIII. ψ -Baptigenin. W. BAKER, R. ROBINSON, and N. M. SIMPSON (J.C.S., 1937, 805—807).— ω -Piperonylresacetophenone (ψ -baptigenetin), Ac_2O , and NaOAc give 7-acetoxy-3':4'-methylenedioxy-2-methylisoflavone, m.p. 198.5°, hydrolysed to the -hydroxy- compound, m.p. 253—254.5°, which forms the -benzyloxy- derivative, m.p. 186°. Condensation of this compound with PhCHO affords 7-benzyloxy-3':4'-methylenedioxy-2-styrylisoflavone, m.p. 199—200.5°, oxidised (KMnO_4) to 7-benzyloxy-3':4'-methylenedioxyisoflavone-2-carboxylic acid, m.p. 179—181°, which with HBr-AcOH is converted into ψ -baptigenin, identical with the natural product (cf. Späth *et al.*, A., 1930, 611; Mahal *et al.*, A., 1935, 90). F. R. S.

Synthesis of brazilin and hæmatoxylin. V. H. APPEL, W. BAKER, H. HAGENBACH, and R. ROBINSON (J.C.S., 1937, 738—744).—Resorcinol and Et indanedionecarboxylate (HCl) give 7-hydroxy-1'-ketoindeno(2':3':3:4)coumarin, m.p. above 340°, of which the Me ether, m.p. 270°, is reduced ($\text{Zn} \cdot \text{AcOH}$) to the H_2 -derivative, m.p. 185—187°, and with NaOH affords 2'-hydroxy-4'-methoxy-3-phenylindan-1-one, m.p. 141.5° (semicarbazone, m.p. 213—214°; Me ether, m.p. 89°). Veratroyl chloride and resorcinol Me_2 ether (AlCl_3) yield 2-hydroxy-4:3':4'-trimethoxybenzophenone, m.p. 140—141°. 7-Methoxy-4-veratryl-, m.p. 151—153°, and 161—163°, obtained from the OH-derivative, is reduced to the -dihydrocoumarin, m.p. 82—83°, and to a product which is hydrolysed and esterified to Et β -veratryl- β -(2-hydroxy-4-methoxyphenyl)propionate, m.p. 113—115°. The ester is converted into β -veratryl- β -(2-benzyloxy-4-methoxyphenyl)propionic acid, m.p. 104—105°, which could not be made to undergo ring-closure. ω -Veratroylresacetophenone 4-veratrate in AcOH-HCl gives 7-veratroyloxy-3':4'-dimethoxyflavone, m.p. 219°, and with the appropriate metallic chloride yields

9-keto-7-veratroyloxy-4':5'-dimethoxybrazylum zincichloride, stannichloride, and ferrichloride; the stannichloride is oxidised (KMnO_4) to veratric acid and hemipinic acid. Pæanol, from resacetophenone and Me_2SO_4 , with veratroyl chloride forms O-veratroylpæanol, m.p. 158—159°, which in presence of NaNH_2 gives ω -veratroylpæanol, m.p. 162—163°, forming brilliant red solutions with metallic chlorides.

F. R. S.

Rottlerin. I. A. MCGOOKIN, F. P. REED, and A. ROBERTSON (J.C.S., 1937, 748—755).—Rottlerin (I), $\text{C}_{33}\text{H}_{30}\text{O}_9$ or $\text{C}_{31}\text{H}_{30}\text{O}_8$, m.p. 212° (cf. Perkin, J.C.S., 1893, 63, 975 *et seq.*; Dutt, A., 1925, 1296; Hoffmann *et al.*, A., 1933, 397), is a highly reactive substance, difficult to obtain pure; some of the results of previous authors have not been confirmed. It gives a Ac_6 derivative (?), m.p. 213°, and is oxidised (KMnO_4) to BzOH ; there is one cinnamyl residue and not two Ph residues. With KOH (I) affords phloroglucinol, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, BzOH , and AcOH , and with $\text{NaOH}\cdot\text{Zn}$, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and *C*-methyl- and -dimethyl- but no trimethyl-phloroglucinol, are obtained. Hydrogenation of (I) yields the H_4 -compound and perhydrorottlerin (II), m.p. 178°. $\text{Ba}(\text{OH})_2$ and (I) lead to rottlerone (III), m.p. 236°, and



some BzCHO ; (III) is reduced to the H_4 -compound (IV), m.p. 172—173° (*Ac* derivative, m.p. 214—215°), methylated to the *Me* derivative, m.p. 102° (*oxime*, m.p. 188°). Perhydrorottlerone, m.p. 166°, may be obtained by reduction of (III) or from (II) and NaOH . Hydrolytic fission of (IV) affords $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and 5:7-dihydroxy-2:2-dimethylehroman. It is suggested that (I) contains the unit shown and that the results disprove the structure suggested by Dutt *et al.* (A., 1928, 643).

F. R. S.

Pyrenium salts. XXVII. 2:4-Diarylnaphthapyrenium salts. W. DILTHEY, W. HÖSCHEN, and O. DORNHEIM (J. pr. Chem., 1937, [ii], 148, 210—216).—*p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHBz}$ and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ in $\text{EtOH}\cdot\text{HCl}$ give (with a substance, m.p. 307—308°) 2-phenyl-4-*p*-anisyl-5:6-naphtha-(1':2')-1:4-pyran, m.p. 205—206° (decomp.). This is converted by $\text{HCl}\cdot\text{MnO}_2$ into the chlorohydrochloride, $\text{C}_{26}\text{H}_{19}\text{O}_2\text{Cl}\cdot\text{HCl}$, which in $\text{COMe}_2\cdot\text{MeOH}\cdot\text{KOAc}$ yields 2-phenyl-4-*p*-anisyl-5:6-naphtha-(1':2')-pyranol, m.p. 197—198° (decomp.) [picrate, new m.p. 210—212° (cf. A., 1935, 1130)]. The perchlorate, m.p. 250° (decomp.), of the last with $\text{AcOH}\cdot\text{H}_2\text{O}_2$ gives 1-*p*-anisoyl- β -naphthyl benzoate (I), m.p. 178°. Attempted synthesis of 1-*p*-anisoyl- β -naphthol from $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ giving only β -naphthyl anisate, m.p. 113—114°, the hydrolysis product of (I) was reduced to *p*-anisyl-2-hydroxy- α -naphthylcarbinol, m.p. 107—108°, also obtained, m.p. 88—89°, from *p*- $\text{C}_6\text{H}_4\cdot\text{Br}\cdot\text{OMe}$ and 2-hydroxy- α -naphthaldehyde. *p*-Anisyl *p*'-methoxystyryl ketone and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ yield 2:4-di-*p*-anisyl-5:6-naphtha-(1':2')-1:4-pyran, m.p. 193—194°, which with $\text{HCl}\cdot\text{MnO}_2$ gives a chloride converted into 2:4-di-*p*-anisyl-

naphtha-1':2'-(5:6)-pyranol, decomp. 180° (perchlorate, m.p. 266—269°; picrate, m.p. 208—211°).

E. W. W.

Polymembered ring systems. VIII. New application of the dilution principle. A. LÜTTINGHAUS and K. ZIEGLER (Annalen, 1937, 528, 155—161).—Ethers $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_n\cdot\text{Br}$ are readily obtained if alkylation is effected in presence of an excess of phenol and dihalide; in this case the alkali compound is present almost exclusively and two-sided reaction of the dihalide is prevented. Cyclisation of the compounds $\text{OR}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_n\cdot\text{Br}$ ($\text{R} = \text{alkali}$) is effected by gradually adding equally conc. solutions of ether and dihalide at the same rate to a fixed vol. of the heated solvent, by adding a cold conc. solution of the pre-prepared K derivative to the heated solvent, or (best) by using an alkali the solubility of which is limited but sufficient to transform the ether as it is added into the reactive alkali compound (*e.g.*, use of K_2CO_3 and boiling amyl alcohol). Resorcinyl κ -bromodecyl ether, m.p. 56°, resorcinol decamethylene ether, $\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_{10}\cdot\text{O}$, b.p. 135—138°/0.5 mm., m.p. 23° {converted by HI (*d* 1.7) in AcOH into *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ and $[\text{CH}_2]_{10}\text{I}_2$ }, and its dimeride, $\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_{10}\cdot\text{O}\cdot\text{C}_6\text{H}_4$, b.p. 200/0.2 mm., m.p. 105—106°, are described.

H. W.

Polymembered ring systems. IX. Pyrocatechol polymethylene ethers. K. ZIEGLER, A. LÜTTINGHAUS, and K. WOHLGEMUTH (Annalen, 1937, 528, 162—180).—Comparison of the yields of cyclic ethers obtained from the alkali salts of pyrocatechol ω -bromoalkyl ethers $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_n\cdot\text{Br}$ ($n = 2$ —10) is rendered somewhat uncertain by the difficulty of exact assessment, but is sufficiently accurate to show the absence of a well-marked min. such as is observed in the readiness of formation of cyclic ketones. Kinetic measurements of the rate of formation of NaBr from $\text{ONa}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_n\cdot\text{Br}$ in EtOH afford an accurate measurement of the rate of cyclisation if the solutions are dil., and difficulties due to alcoholysis can be overcome by use of a large excess of NaOEt ; the limit of applicability of the method appears to be reached when $n = 10$. The rate diminishes rapidly from the 6- through the 7- to the 8-ring, and then continuously but less rapidly as would be expected in a homologous series from which steric influences are absent. This absence is ascribed to the 2 O and possibly also to the 2 C of the C_6H_6 ring, to all of which H is not attached. The following ethers are obtained by the action of an excess of the alkylene dibromide on pyrocatechol and NaOEt (mol. ratio, 3:1): *o*-hydroxyphenyl γ -bromopropyl, b.p. 101°/0.25 mm., m.p. 59°, δ -bromobutyl, b.p. 117°/0.25 mm., ϵ -bromoamyl, b.p. 132°/0.25 mm., ζ -bromohexyl, b.p. 150°/0.17 mm., η -bromoheptyl, m.p. 32°, θ -bromo-octyl, ι -bromononyl, b.p. 165°/0.25 mm., m.p. 19°, κ -bromodecyl, b.p. 180°/0.24 mm. *o*- $\text{C}_6\text{H}_4(\text{OH})_2$, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$, and NaOEt afford *o*-hydroxyphenyl β -hydroxyethyl ether, b.p. 128°/0.7 mm., m.p. 100—101°, transformed by PBr_3 and $\text{C}_2\text{H}_5\text{N}$ into *o*-hydroxyphenyl β -bromoethyl ether, b.p. 95°/0.25 mm. Gradual addition of these to a mixture of K_2CO_3

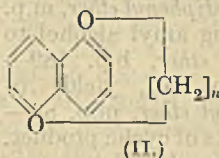
and boiling amyl alcohol affords the following *o*-dioxynaphthalenes: ethylene-, trimethylene-, b.p. 103°/10 mm.; tetramethylene-, b.p. 112°/10 mm.; pentamethylene-, b.p. 122°/10 mm.; hexamethylene-, b.p. 140°/10 mm., m.p. 38°; heptamethylene-, b.p. 156°/10 mm.; m.p. 17—18°; octamethylene-, b.p. 171°/10 mm., m.p. 46°; nonamethylene-, b.p. 185°/10 mm., m.p. 58°; decamethylene-, b.p. 197°/10 mm. H. W.

Polymembered ring systems. X. New dihydroxybenzene and dihydroxynaphthalene derivatives. A. LÜTTRINGHAUS (Annalen, 1937, 528, 181—210).—*p*-C₆H₄(OH)₂ readily yields a polymethylene ether with 10, much less readily with 8, CH₂ groups whereas similar compounds with 7 or 6 CH₂ groups could not be obtained. From *m*-C₆H₄(OH)₂ an ether with 7 CH₂ groups is obtained with some difficulty, and the similar substance with 6 CH₂ is possibly formed in very small amount. 1:5- and 2:6-C₁₀H₆(OH)₂ afford ethers with 10 CH₂, but a compound with 8 CH₂ could not be derived from the latter. Consideration of at. distances in conjunction with readiness of ring formation appears to indicate a great stability of the plane or slightly bent form of the C₆H₆ nucleus, and to show that more energy is required for the deformation of a single mol. than can be derived from the kinetic mol. energy at 100—150°. Similarly, the energy required for alteration of the inclination of the 2 plane C₆H₆ nuclei in C₁₀H₈ towards one another is at any rate in excess of the mean energy of activation of processes occurring with reasonable rapidity between 100° and 150°. The very high mol. depression of the f.p. shown by various cyclic ketones is not shared with these complex ethers, but the introduction of a C₆H₆ nucleus into the ring system does not alter the general character of the odour in spite of the presence of a 2 ethereal O atoms.

Quinol is converted by Br·[CH₂]₁₀·Br and KOH in boiling EtOH into *quinol mono-κ-bromodecyl ether*, m.p. 76–77°, cyclised by K₂CO₃ in boiling amyl alcohol to *quinol decamethylene ether* (I), b.p. 120—125°/0.2 mm., m.p. 63°, in 79% yield. (I) does not react with MgMeI and is converted by 48% HBr in boiling Ac₂O into *p*-C₆H₄(OH)₂ and Br·[CH₂]₁₀·Br. *Quinol mono-θ-bromo-n-octyl ether*, m.p. 65°, is transformed into *quinol octamethylene ether*, b.p. 134°/0.8 mm., m.p. 65° (yield 18%), and the *dimeric octamethylene ether*, b.p. 235°/0.5 mm., m.p. 99°. Attempted cyclisation of *quinol mono-η-bromo-n-heptyl ether*, b.p. 164°/about 0.02 mm., m.p. 33°, gives small amounts of non-cryst. material volatile with steam, *quinol mono-η-amyloxy-n-heptyl ether*, b.p. 192—196°/0.8 mm., and the *dimeric heptamethylene ether*, C₂₆H₂₆O₄, m.p. 113°. *Quinol mono-ζ-bromo-n-hexyl ether* has m.p. 57°. *Resorcinol mono-η-bromo-n-heptyl ether*, b.p. 176°/0.04 mm., gives *resorcinol heptamethylene ether*, m.p. 109—109.5°, in 10% yield. Attempted cyclisation of *resorcinol mono-ζ-bromo-n-hexyl ether* gives a product which reacts with MgMeI, *dimeric resorcinol hexamethylene ether*, m.p. 114°, and *resorcinol mono-ζ-amyloxy-n-hexyl ether*, b.p. 173—176°/0.4 mm. *Resorcinol β-β'-bromo-ethoxyethyl ether*, b.p. 146°/0.06 mm., is transformed by K₂CO₃ in boiling amyl alcohol into the *dimeric ether*,

$$\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \cdot [\text{CH}_2]_2 \cdot \text{O} \cdot [\text{CH}_2]_2 \cdot \text{O} \\ \text{O} \cdot [\text{CH}_2]_2 \cdot \text{O} \cdot [\text{CH}_2]_2 \cdot \text{O} \end{array} \text{C}_6\text{H}_4, \quad \text{m.p. } 164^\circ.$$

Quinol di-n-butyl, m.p. 46°, and *di-n-amyl ether*, b.p. 192°/15 mm., m.p. 45°, are described. 1:5-C₁₀H₆(OH)₂ is transformed by Br·[CH₂]₁₀·Br and KOH in boiling EtOH into 1-hydroxy-5-κ-bromo-n-decoxynaphthalene, m.p. 70.5°, cyclised to 1:5-dihydroxynaphthalene decamethylene ether



(II; *n* = 10), b.p. 160—164°/0.05 mm., m.p. 105°, in 61.5% yield. 1-Hydroxy-5-θ-bromo-n-octoxynaphthalene has m.p. 64°. 2-Hydroxy-6-κ-bromo-n-decoxynaphthalene, m.p. 96°, gives 1:6-dihydroxynaphthalene decamethylene ether, b.p. 130—135°/0.02 mm., m.p. 89—90°, in 22% yield. H. W.

Polymembered ring systems. XI. Form of the diphenyl and diphenylmethane molecules. A. LÜTTRINGHAUS (Annalen, 1937, 528, 211—222).—Considerations of at. distances indicate that, provided distortion of the mol. does not occur, the conversion of *p*-OH·C₆H₄·C₆H₄·OH·*p*' into an un- or do-decamethylene ether should occur. The failure to obtain a decamethylene ether is regarded as strong confirmation of the extended form and fixity of the Ph₂ system. Cyclisation of the somewhat similar CH₂(C₆H₄·OH·*p*)₂ to a heptamethylene ether is possible. Gradual addition of KOH·EtOH to *p*-OH·C₆H₄·C₆H₄·OH·*p*' and Br·[CH₂]₁₀·Br in boiling EtOH affords *p*-hydroxy-*p*'-κ-bromo-n-decoxydiphenyl, m.p. 127—128°, converted by K₂CO₃ in boiling amyl alcohol into *p*-hydroxy-*p*'-κ-amyloxydecoxydiphenyl, m.p. 111—113°. *p*-Hydroxy-*p*'-κ-bromo-n-decoxydiphenylmethane, m.p. 80—81°, is converted into *pp'*-dihydroxydiphenylmethane decamethylene ether, b.p. 206°/0.3 mm., m.p. 76° (yield 68%), which does not react with MgMeI, gives I·[CH₂]₁₀·I when treated with HI (d 1.7) in boiling Ac₂O, and affords CH₂(C₆H₄·OH·*p*)₂ when heated with KOH·NaOH at 300° in absence of air. *p*-Hydroxy-*p*'-θ-bromo-n-actoxydiphenylmethane, m.p. 65—66°, yields *pp'*-dihydroxydiphenylmethane octamethylene ether, b.p. 168—170°/0.2 mm., m.p. 85—86°, in 29% yield whilst *p*-hydroxy-*p*'-η-bromo-n-heptoxydiphenylmethane, m.p. 78°, affords *pp'*-dihydroxydiphenylmethane heptamethylene ether, m.p. 120° (5%), and the *dimeric ether*, CH₂<C₆H₄·O·[CH₂]₇·O·C₆H₄>CH₂, m.p. 136.5°.

H. W.

Polymembered ring systems. XII. Valency angle of the oxygen atom in derivatives of diphenyl ether. A. LÜTTRINGHAUS (Annalen, 1937, 528, 223—233).—If the valency angle 110° is ascribed to O, close parallelism between ease of formation of cyclic ether with O(C₆H₄·OH·*p*)₂ and CH₂(C₆H₄·OH·*p*)₂ is to be expected. Since this is not observed, it appears that the angle of O is much more strongly affected by substituents than that of C^{IV} and cannot be regarded as const. The possibility that ·O· and ·CH₂· are so closely similar that corresponding compounds are isomorphous has been partly realised in the open systems OPh·CH₂Ph and (·CH₂Ph)₂ and is completely realised in the fixed systems fluorene and diphenylene oxide in which close similarity of valency angle is enforced. CH₂Ph₂ and Ph₂O, however, give a pronounced eutectic and there is evidence of

limited miscibility. Addition of KOH-EtOH to $O(C_6H_4 \cdot OH \cdot p)_2$ and $Br[CH_2]_2 \cdot Br$ in boiling EtOH gives *p*-hydroxy-*p*- κ -bromo-*n*-decoxydiphenyl ether, m.p. 90.5°, cyclised by K_2CO_3 in boiling amyl alcohol to *pp'*-diphenyl oxide decamethylene ether, b.p. 189—195°/0.5 mm., m.p. 79—80°, in 36% yield. *p*-Hydroxy-*p'*- θ -bromo-*n*-octoxydiphenyl ether, m.p. 83—84°, gives at most, minimal amounts of cyclic product. *p*-Hydroxy-*p'*- ζ -bromo-*n*-hexoxydiphenyl ether, m.p. 78°, affords the dimeric product, $C_{36}H_{40}O_6$, m.p. 142°.

H. W.

Molecular compounds of pyrrole derivatives. M. DEŽELIĆ (Bull. Soc. Chim. Yougoslav., 1936, 7, 91—113).—The fusion diagrams suggest 1:1 compounds in the systems Et 3-acetyl-2:4-dimethylpyrrole-5-carboxylate (I)— $CH_2Cl \cdot CO_2H$ (II), transition point (t.p.) 85.3°, —PhOH, t.p. 93°, —picric acid (III), —salicylic acid (IV), t.p. 98°, and Et 3-aldehyde-2:4-dimethylpyrrole-5-carboxylate (V)—(II), t.p. 74.5°, —(IV), m.p. 135°, —(III), t.p. 97°, —*o*- (VI), m.p. 114°, and — $m\text{-}C_6H_4(OH)_2$ (VII), m.p. 111°, Et 4-aldehyde-2:4-dimethylpyrrole-3-carboxylate (VIII)—(IV), m.p. 111.5°, —(VII), t.p. 98°, and —quinol (IX), m.p. 117.5°, and 2:1 compounds in the systems (I)—(IV), t.p. 113°, —(VI), t.p. 108.5°, —(VII), m.p. 139°, and —(IX), t.p. 108.5°, Et 2:5-dimethylpyrrole-5-carboxylate (X)—(III), t.p. 100°, (V)—(IX), m.p. 142°, and (VIII)—(IV), t.p. 111°. Compound formation is not observed in the systems (I), (V), (VIII), or (X)—AcOH, —($CH_2 \cdot CO_2H$)₂, —BzOH, (X)—(II), —PhOH, —(IV), —(VI), —(VII), —(IX), and —benzoquinone, and (VIII)—(VI).

R. T.

Some furan ketones with several double linkings (II) and some ethylenic ketones with a pyrrole nucleus. N. MAXIM and I. COPUZEANU (Bull. Soc. chim., 1936, [v], 3, 2251—2256).—Furfurylideneacetone with *p*- $C_6H_4Me \cdot CHO$ and EtOH-NaOH gives *furfurylidene*-(*p*-methylbenzylidene)acetone, m.p. 85°, b.p. 237°/18 mm. Similarly, *furfurylidene*-(*o*-nitrobenzylidene)acetone, m.p. 104° (corresponding m., m.p. 125°, and *p*., m.p. 159—160°, — NO_2 and *o*-Cl, m.p. 80°, —compounds), has been prepared. The following have been prepared by treating pyrrol Me ketone with the appropriate aldehyde, EtOH, and NaOH: *p*-methyl-, m.p. 152—153°, *o*-chloro-, m.p. 124°, *p*-methoxy-, m.p. 137°, *m*-nitro-, m.p. 203—204°, *p*-nitro-, m.p. 204°, *p*-dimethylamino-, m.p. 199—200°, —benzylidenemethyl pyrrol ketone.

H. G. M.

Diaminomethane and its derivatives. II. α -Aminopiperidine and the products of reduction of α -aminopyridine. III. Hydrolysis of diacetyl- α -aminopiperidine and the pseudo-dipiperidine of Ahrens. A. V. KIRSANOV and J. N. IVASTCHENKO (Bull. Soc. chim., 1936, [v], 3, 2279—2288, 2289—2295).—II. Contrary to the conclusions of previous workers (cf. Tschitschabin *et al.*, A., 1930, 925), reduction of 2-aminopyridine (I) with Na-EtOH yields NH_3 , $C_5H_{11}N$, and cadaverine, but no 2-aminopiperidine, considered to be too unstable for isolation. A mechanism for the formation of the foregoing products is given. Catalytic reduction (H_2 -Pt) of the Ac derivative of (I), in presence of Ac_2O —AcOH, gives NN'-diacetyl-2-aminopiperidine (II), m.p. 122—123°, and similarly

NN-diphenyl-2-aminopyridine in AcOH is hydrogenated to NN-diphenyl- α -aminopiperidine, m.p. 131—133°.



in equilibrium with (III).

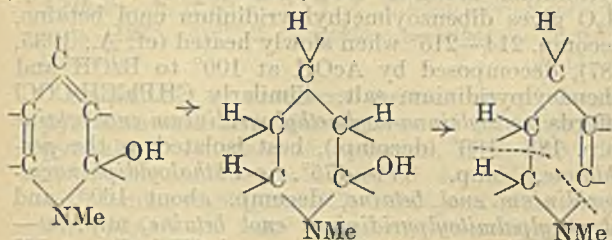
H. G. M.

Aliphatic polyamines. V. J. VAN ALPHEN (Rec. trav. chim., 1937, 56, 529—534).— α -Dibromopentane and $(CH_2 \cdot NH_2)_2$ in hot EtOH-KOH give 1- β -aminoethylpiperidine [picrate, m.p. 221° (Gabriel, A., 1921, i, 58, gives m.p. 214—215°); Bz, m.p. 59°, and benzylidene derivative, b.p. 205°/38 mm., reduced by Na-EtOH to the *N*-benzyl derivative, b.p. 178°/20 mm. (hydrochloride, +2H₂O, decomp. 210°; picrate, m.p. 60°; phenylcarbamyl, m.p. 156°, and phenylthiocarbamyl derivative, m.p. 148°)], which with PhNCO and PhNCS gives, respectively *s*-phenyl- β -1-piperidinoethyl-carbamide, m.p. 270°, and —thiocarbamide, m.p. 261°, and with CS₂—EtOH affords the internal salt $C_5H_{10} > NH \cdot [CH_2]_2 \cdot NH \cdot CS \cdot S$, m.p. 126—128° (decomp.), converted at 140—170° into *s*-di- β -1-piperidinoethylthiocarbamide, m.p. 92°.

J. W. B.

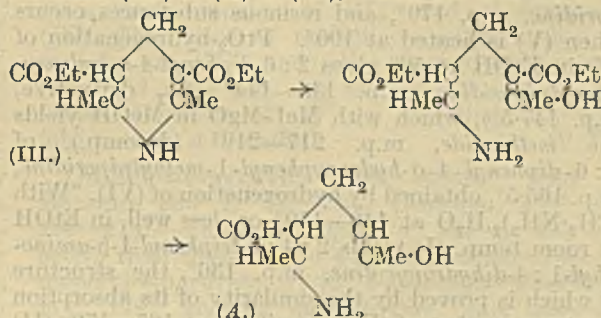
Derivatives of *p*-aminobenzenesulphonamide in the treatment of streptococcal infection in mice. W. H. GRAY, G. A. H. BUTTLE, and D. STEPHENSON (Biochem. J., 1937, 31, 724—730).—A no. of derivatives of *p*-aminobenzenesulphonamide (I) have been prepared and tested for toxicity and protective effect against infection with hæmolytic streptococci. A no. of the compounds tested are tolerated in larger doses than (I). The following are described: *p*-acetamidobenzenesulphonylcyclohexylamide, m.p. 224°; *p*-aminobenzenesulphonylcyclohexylamide hydrochloride, m.p. 227°; *p*-acetamidobenzenesulphonyl-*p'*-sulphonamidophenylamide, m.p. 280°; *p*-aminobenzenesulphonyl-*p'*-sulphonamidophenylamide hydrochloride, m.p. 224°; *p*-aminobenzenesulphonpiperidide, m.p. 164°; 2'-pyrrolidone-5'-carboxy-4-aminobenzenesulphonamide, m.p. 262°, optically inactive; 4:4'-disulphonamidodiazaminobenzene, m.p. 172°; *p*-cinnamylidene-, m.p. 215°, *p'*-methoxybenzylidene-*p*., m.p. 200°, 3':4'-dimethoxybenzylidene-4-, m.p. 196°, 3':4'-diethoxybenzylidene-4-, m.p. 216°, 3':4'-methylenedioxybenzylidene-4-, m.p. 219°, 3'-nitrobenzylidene-4-, m.p. 173°, 6'-nitro-3'-hydroxybenzylidene-4-, m.p. 197°, *p'*-dimethylamino-benzylidene-*p*., m.p. 229°, and *p*-furfurylidene-, m.p. 196°, —aminobenzenesulphonamides; and *p*-sulphonamidoglucoseanil, m.p. 210°. *p*-Aminobenzenesulphonyldiethylamide and its Ac derivative previously mentioned but not described by Fournau *et al.* (A., 1936, 1029) have m.p. 105° and 82°. A more convenient prep. of azobenzene-*p*-sulphonamide than that of Skandarow (1870) is described. E. A. H. R.

Tetrahydropyridine series. O. MUMM [with W. BUTTENSCHÖN, W. FRIEDRICHSEN, and W. GRASSMANN] (Annalen, 1937, **529**, 115—141).—Tetrahydropyridine derivatives are accessible by hydrogenation of C_5H_5N derivatives in which each atom in the ring bears a substituent; quaternary salts are the best starting materials and reaction probably proceeds by way of the ψ -base:



These highly substituted H_4 -compounds are fairly stable; ring-opening occurs, though with less ease than in the H_2 -series, and a remarkable thermal decomp., indicated by the dotted line, into $CHR:NMe$ and a butadiene derivative is characteristic. Less fully substituted H_4 -derivatives are obtained by disproportionation of H_2 -compounds; they are less stable, particularly to O_2 . Hydrogenation (colloidal Pt or PtO_2 ; 2 atm.) of Et_2 collidinedicarboxylate methosulphate in H_2O gives a 91% yield of Et_2 N-methyltetrahydrocollidine-3:5-dicarboxylate, b.p. $164^\circ/12$ mm. (blue fluorescence; *picrate*, m.p. 131°), hydrolysed by conc. HCl at 120° with loss of CO_2 and ring-fission to β -methylamino- δ -methylheptan- ζ -one- γ -carboxylic acid (hydrochloride, m.p. 148° ; *picrate*, m.p. 187 — 188° ; also obtained less well by hot 20% KOH-EtOH) and decomposing, when distilled at 760 mm., into $CHMe:NMe$ (detected by hydrolysis to NH_2Me and $MeCHO$) and Et γ -carbethoxy- β -methyl- $\Delta^{\alpha\gamma}$ -hexadienoate (I), b.p. about $142^\circ/16$ mm. Hydrolysis of (I) by hot 20% KOH-EtOH gives two (?) stereoisomeric forms, m.p. 156° (decomp.) (often 149° or oily) and 196° (decomp. about 270°), of the corresponding dicarboxylic acid; both forms absorb 2 H_2 (PtO_2 ; AcOH), but only the second gives smoothly β -methyl- α -ethylglutaric acid, m.p. 100 — 101° , which is also obtained by way of its Et_2 ester, b.p. $134^\circ/18$ mm., by hydrogenation of (I). Hydrogenation (PtO_2 ; EtOH) of Et_2 4-phenyl-lutidinedicarboxylate methosulphate leads to partial hydrogenation of the Ph and isolation of the impure 4-phenyltetrahydro-ester, b.p. about 205 — $220^\circ/14$ mm., which at about $300^\circ/760$ mm. gives Et γ -carbethoxy- β -phenyl- $\Delta^{\alpha\gamma}$ -hexadienoate, b.p. 196 — $204^\circ/14$ mm., converted, by the methods used for (I), into the corresponding dicarboxylic acid, m.p. 157° (decomp.), and β -phenyl- α -ethylglutaric acid, m.p. 166° (Et_2 ester, b.p. 178 — $182^\circ/11$ mm.). Hydrogenation (colloidal Pt; 2 atm.) of Et_2 4-benzyl-lutidinedicarboxylate methosulphate gives Et_2 4-benzyl-N-methyl- Δ^2 -tetrahydrolutidinedicarboxylate, m.p. 51° (platinichloride, m.p. 198 — 200° ; perchlorate, m.p. 177° ; yellowish-green fluorescence), and (?) the Δ^3 -ester, an oil (only faintly fluorescent), converted into the solid isomeride by ultra-violet light; conc. HCl at 110° gives 4-benzyl-N-methyltetrahydrolutidine-3:5-dicarboxylic acid, m.p. 176° (hydrochloride, m.p. 181°), and β -

methylamino- δ -benzylheptan- ζ -one- γ -carboxylic acid, m.p. 206° (decomp.); distillation/vac. gives Et γ -carbethoxy- β -benzyl- $\Delta^{\alpha\gamma}$ -hexadienoate, b.p. $198^\circ/17$ mm., and thence the corresponding dicarboxylic acid, m.p. 131° , and Et_2 β -benzyl- α -ethylglutarate, b.p. $190^\circ/16$ mm. Et_2 dihydrolutidinedicarboxylate (II) and HCl-AcOH give Et_2 lutidinedicarboxylate, Et_2 tetrahydrolutidinedicarboxylate (III), m.p. 89° , b.p. 161 — $165^\circ/0.8$ mm. [considered by Knoevenagel and Fuchs (A., 1902, i, 565) to be the H_6 -ester; NO-derivative, m.p. 54°], and Et Δ^5 -tetrahydrolutidine-3-carboxylate (IV), b.p. 108 — $110^\circ/12$ mm., $235^\circ/760$ mm. (mercuri- and platinichloride, m.p. 138° ; *picrate*, m.p. 120°); the amount of (IV) increases with time at the expense of (III) and it arises from (III) by the reactions (III) \rightarrow (A) \rightarrow (IV), which are also realised



from pure (III). The structure of (IV) is proved by hydrogenation (colloidal Pt; AcOH; 1 H_2 absorbed) to Et hexahydrolutidine-3-carboxylate, b.p. $102^\circ/14$ mm., $219^\circ/760$ mm. (mercuri- and auri-chloride, m.p. 147° ; perchlorate, m.p. 163°). Hydrogenation (colloidal Pt) of (II) or (III) gives Et_2 hexahydrolutidinedicarboxylate, b.p. $154^\circ/12.5$ mm., $292^\circ/770$ mm., m.p. 58 — 59° [platinichloride, m.p. 208 — 210° (decomp.); *picrate*, m.p. 154°]. (III) is autoxidised in air; it absorbs 1 O_2 at room temp. to give Et_2 2-hydroxymethylene-6-methylpiperidine-3:5-dicarboxylate, b.p. 141 — $144^\circ/0.7$ mm., which absorbs 1 H_2 catalytically and at 100° absorbs a further 2 O_2 to give the oily 2-carboxylic acid. R. S. C.

Formation of pyridines from 1:5-[$\alpha\epsilon$]-diketones. K. W. MERZ and H. RICHTER (Arch. Pharm., 1937, **275**, 294—317).—Benzylidene- (I) and salicylidene-diacetophenone (II) [$\alpha\gamma\epsilon$ -triphenyl- and $\alpha\epsilon$ -diphenyl- γ -o-hydroxyphenyl-penta- $\alpha\epsilon$ -dione] differ in their mode of condensation with NH_3 and primary bases. Dry NH_3 -EtOH at room temp. converts (I) into 2:4:6-triphenylpyridine (III) [dibromide hydrobromide, m.p. 209 — 210° (decomp.)], converted into (III) by C_5H_5N ; *picrate*, m.p. 193.5°], δ -imino- $\beta\delta$ -diphenylvalerophenone (IV), m.p. 111 — 116° , and a N-free substance, m.p. 246 — 248° . (IV) is an intermediate product in this reaction and under other conditions forms the main product; it gives (III) when treated with acid or alkali, by spontaneous decomp., and when heated at 120° . Formation of (III) instead of the dihydropyridine is due to dehydrogenation, which leads also to some hydrogenation of (I) during the reaction; with NH_2Et (I) gives (III), evolution of C_2H_6 taking place instead of the dehydrogenation. With $C_6H_5(NO_2)_2OH$ in hot EtOH (IV) affords 2:4:6-triphenyl-1:4-dihydropyridin

picrate, m.p. 155°, without dehydrogenation. In AcOH at 100° (IV) affords by disproportionation (III) and 2:4:6-triphenyltetrahydropyridine, m.p. 125-5°. With H_2 -Pt in EtOH at 45-50° (IV) yields ϵ -amino- α -triphenylpentan- α -ol, an oil [hydrochloride, m.p. 274-275° (decomp.); H oxalate, + α EtOH, m.p. 115-5°; carbamide derivative, m.p. 171-172°; with Ac_2O gives 1-acetyl-2:4:6-triphenylpiperidine, m.p. 161°]. Condensation of (II) with NH_3 and NH_2R occurs without dehydrogenation, giving 2:6-diphenyl-4-o-hydroxyphenyl-1:4-dihydropyridine (V), m.p. 145-5-146°, 1-methyl- (VI), m.p. 121°, and 1-ethyl-2:6-diphenyl-4-o-hydroxyphenyl-1:4-dihydropyridine, m.p. 128-129°, hydrolysed to the starting materials by hot AcOH or mineral acid. Disproportionation to 2:6-diphenyl-4-o-hydroxyphenylpyridine, m.p. 179°, and resinous substances occurs when (V) is heated at 190°. PtO_2 -hydrogenation of (V) in EtOH at 50° gives 2:6-diphenyl-4-o-hydroxyphenylpiperidine, m.p. 143-144° (Bz_2 derivative, m.p. 147-5°), which with $MeI-MgO$ in MeOH yields the methiodide, m.p. 217-219° (decomp.), of 2:6-diphenyl-4-o-hydroxyphenyl-1-methylpiperidine, m.p. 165-5°, obtained by hydrogenation of (VI). With $(CH_3NH_2)_2H_2O$ at 140-150° or, less well, in EtOH at room temp. (I) yields 2:4:6-triphenyl-1- β -aminoethyl-1:4-dihydropyridine, m.p. 136°, the structure of which is proved by the similarity of its absorption spectrum to that of (VI); similarly at 165-170° (II) affords 2:4-diphenyl-4-o-hydroxyphenyl-1- β -aminoethyl-1:4-dihydropyridine, m.p. 150°. With $N_2H_4 \cdot H_2O$ at 130° (I) gives 1-amino-2:4:6-triphenyl-1:4-dihydropyridine, m.p. 158-5-159°. R. S. C.

(A) Hydrogenation of pyridine and pyridine bases under pressure in presence of nickel-silica gel catalysts. M. I. USCHAKOV and A. I. BRONEVSKI. (B) Relative velocity of catalytic hydrogenation of pyridine and picolines in the hydrogenation of mixtures of pyridine bases. M. I. USCHAKOV and E. V. JAKOVLEVA (J. Gen. Chem. Russ., 1937, 7, 750-752, 753-758).—(A) The velocity of hydrogenation ($Ni-SiO_2$ gel catalyst) at 150-200°/50-100 atm. falls in the series $C_5H_5N > \alpha > \beta > \gamma$ -picoline.

(B) C_5H_5N and α -picoline can be separated from their mixtures with β - and γ -picoline by fractional hydrogenation, as piperidine and α -piperidine, as above, or by hydrogenation of the hydrochlorides, using a Pt catalyst. R. T.

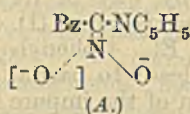
Direct iodination of pyridine. Z. RODEWALD and E. PLAŽEK (Ber., 1937, 70, [B], 1159-1162).— C_5H_5N and I do not react when heated in a sealed tube under varied conditions. Treatment of molten $C_5H_5N \cdot HCl$ with I gives penta-iodopyridine (I) in very small yields whilst most of the C_5H_5N remains unattacked. (I) and 3:5-di-iodopyridine (II), m.p. 173° (constitution established by conversion into 3:5-diaminopyridine), are formed when the vapours of C_5H_5N and I are heated. Replacement of I by ICl does not give appreciable improvement and considerable amounts of 2-chloropyridine result; addition of Hg or Fe salts is without influence. 2-Pyridyl-1-pyridinium iodide is obtained from $C_5H_5N \cdot HCl$ and I or ICl. The best yield results by the

action of I in fuming H_2SO_4 (50% SO_3), whereby 3-iodopyridine (III) (yield 18%) and (II) are produced. 2- or 4-Iodopyridine could not be thus obtained and (III) could not be converted into (II). H. W.

Enol betaines. V. Reactions with acid chlorides. F. KRÖHNKE (Ber., 1937, 70, [B], 1114-1117; cf. this vol., 208, 209).—Agitation of phenacylpyridinium bromide, $BzCl$, and K_2CO_3 in $CHCl_3-H_2O$ gives dibenzoylmethylpyridinium enol betaine, decomp. 214-215° when slowly heated (cf. A., 1935, 987), decomposed by AcOH at 100° to $BzOH$ and phenacylpyridinium salt. Similarly $CHPh \cdot CH \cdot COCl$ affords benzoylcinnamoylmethylpyridinium enol betaine m.p. 185-186° (decomp.), best isolated as the perchlorate, m.p. 174-175°. o-Phthaloyldiphenacylpyridinium enol betaine, decomp. about 160°, and phenacylpalmitoylpyridinium enol betaine, m.p. 90-92°, are described. Quinoline and $CHBz_2Br$ at 36° slowly yield dibenzoylmethylquinolinium enol betaine, decomp. about 240°. p-Chloro- and p-bromo-phenacylpyridinium enol betaine yield additive compounds, m.p. 85° after slight decomp. and m.p. 80-90°, respectively, with $BzCN$. H. W.

Coloured oximinobetaines. F. KRÖHNKE and H. KÜBLER (Ber., 1937, 70, [B], 1117-1120).—Treatment of phenacylpyridinium bromide (I) in 50% EtOH with an excess of amyl (II) or Et nitrite and $N-NaOH$ at 0° gives the unstable basic bromide (III), m.p. about 55° (decomp.), transformed by $N-HBr$ into oximinophenacylpyridinium bromide (IV), $OH \cdot N \cdot CBz \cdot N(C_5H_5)Br$, m.p. 147° (decomp.) [corresponding perchlorate, m.p. 115° (decomp.)], also obtained directly from (I), $NaNO_2$, and $N-HBr$ at 0°, or from (I) and (II) in EtOH at 0° or when heated. (III) is converted by 1-4N- K_2CO_3 at 35° into labile oximinophenacylpyridinium enol betaine (V), m.p. 46-48° (decomp.) varying with the mode of heating, which rapidly decomposes on contact with glass or earthenware but can be preserved on agate. It is transformed by the requisite amounts of HBr into (III) or (IV). When triturated with abs. EtOH (V) is transformed into red needles, m.p. about 42° (decomp.). When heated with 0.5-1N- $NaOH$ (V) passes into a more stable, yellow betaine, decomp. about 61°. The constitution A for (V) is supported by the analogous formation of oximinophenacylisoquinolinium bromide, m.p. 161-162° (decomp.), and its conversion into the more stable oximinophenacylisoquinolinium enol betaine, m.p. 69-70° (decomp.). The betaine derived from oximino-p-chlorophenacylpyridinium bromide, m.p. 125° (decomp.), is more sensitive than the corresponding Cl-free derivative. p-Nitrobenzylisoquinolinium bromide appears to be transformed by $NaOH$ (not Na_2CO_3) and $CHCl_3$ into the corresponding aci-nitro-betaine. H. W.

Synthesis of 2:4-dihydroxyquinoline derivatives from malonic esters and aromatic amines. A. MEYER and P. HEIMANN (Compt. rend., 1937, 204, 1204-1206).—Arylamides of malonic esters, heated with paraffin oil to 250°, lose H_2O and give 2-hydroxy-4-alkoxyquinolines; under the same conditions, arylamides of C-substituted malonic esters lose EtOH



yielding 2:4-dihydroxy-3-alkylquinolines, whilst PCl_5 as condensing agent gives 2:3-dichloro-4-alkoxyquinolines. The following are prepared: 6-chloro-2-hydroxy-4-ethoxy-, m.p. 91° , 2-hydroxy-4-ethoxy-6-methyl-, m.p. 138° , 2-hydroxy-4-ethoxy-8-methyl-, m.p. 190° , 6-chloro-2:4-dihydroxy-3-ethyl-, m.p. 264° , 2:4-dihydroxy-8-methyl-3-ethyl-, m.p. 218° , 4:6-dichloro-2-hydroxy-, m.p. 138° , 2:3:8-trichloro-4-ethoxy-, m.p. 63.5° , 2:3:4:6-tetrachloro-8-methoxy-, m.p. 127° , and 2:4-dichloro-8-methoxy-, m.p. 92° quinoline.

J. D. R.

Reactivity of methoxy-derivatives of 3-nitropyridine and new derivatives of 3:4-pyridinopyrazine. O. BREMER (Annalen, 1937, **529**, 290—298).—Successive treatments of 4-pyridone nitrate with fuming H_2SO_4 and $\text{PCl}_5\text{-POCl}_3$ and of the product with MeOH at $>20^\circ$ give 3-nitro-4-methoxypyridine hydrochloride, converted by aq. K_2CO_3 into 3-nitro-4-methoxypyridine (I), m.p. 75° . $\text{CHNa}(\text{CO}_2\text{Et})_2$ and (I) in boiling abs. EtOH give Et_2 3-nitro-4-methoxypyridylmalonate, b.p. $157^\circ/3$ mm., hydrolysed by boiling 18% HCl to 3-nitro-4-methylpyridine, b.p. $85^\circ/3$ mm. [hydrochloride, m.p. 176° (decomp.)], transformed by PhCHO and piperidine at $160\text{--}170^\circ$ into 3-nitro-4-stilbazole, m.p. $114\text{--}115^\circ$. Diazotisation of 3-amino-4-methoxypyridine followed by treatment with Cu powder-CuCl yields 3-chloro-4-methoxypyridine, b.p. $83\text{--}84^\circ/3$ mm. (hydrochloride). 5-Bromo-3-nitro-4-hydroxypyridine and PCl_5 containing a little POCl_3 at 160° give 4-chloro-5-bromo-3-nitropyridine (II), m.p. $49\text{--}50^\circ$, which with $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$ at 100° gives 5-bromo-3-nitro-4- β -hydroxyethylaminopyridine, m.p. $120\text{--}121^\circ$. (II) and NaOMe in abs. MeOH afford 5-bromo-3-nitro-4-methoxypyridine, m.p. $39\text{--}40^\circ$; 5-bromo-3-nitro-6-methoxypyridine (III), m.p. 89° , is obtained similarly. At $170\text{--}180^\circ$ (I) passes into 3-nitro-1-methyl-4-pyridone, m.p. 220° . $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$ and (III) at 100° give 5-bromo-3-nitro-6- β -hydroxyethylaminopyridine, m.p. 136° . 3-Amino-4-butyraminopyridine and $\text{Et}_2\text{C}_2\text{O}_4$ at 170° give 2-hydroxy-3-keto-4-butyl-3:4-dihydropyridino-(3':4')-5:6-pyrazine, m.p. 256° ; 2-hydroxy-3-keto-4-phenyl-3:4-dihydropyridine-(3':4')-5:6-pyrazine, m.p. $>325^\circ$, is obtained similarly from 3-amino-4-anilinopyridine.

H. W.

Esters of nicotinic acid. J. L. GOLDFARB (J. Appl. Chem. Russ., 1937, **10**, 515—520).—The following esters have been prepared from nicotiny chloride and the appropriate alcohol: benzyl, b.p. $179^\circ/9$ mm. (methiodide, m.p. $159\text{--}160^\circ$; hydrochloride, m.p. $72\text{--}74^\circ$; picrate, m.p. $156\text{--}157^\circ$), furfuryl, b.p. $152^\circ/6$ mm., m.p. $32\text{--}34^\circ$ (methiodide, m.p. 137° ; hydrochloride, m.p. 130° ; picrate, m.p. 128°), β -naphthyl, b.p. $197\text{--}199^\circ/1$ mm., m.p. 160° (methiodide, m.p. $191\text{--}194^\circ$; hydrochloride, m.p. $191\text{--}194^\circ$; picrate, m.p. $177.5\text{--}178.5^\circ$), and cyclohexyl, b.p. $150^\circ/7$ mm. (methiodide, m.p. $114.5\text{--}115.5^\circ$; hydrochloride, m.p. 120° ; picrate, m.p. 116°), nicotinate.

R. T.

Xanthurenic acid. I—III. Xanthurenic acid, kynurenine acid, and kynurenine. L. MUSAJO (Gazzetta, 1937, **67**, 165—171, 171—178, 179—188).—I. Urine of albino rats on a hyperprotein diet (almost entirely fibrin) contains the Na salt

($+2\text{H}_2\text{O}$) of xanthurenic acid (I), $\text{C}_{10}\text{H}_7\text{O}_4\text{N}$ [Me ester (II), m.p. 262°], which gives an intense green colour with aq. FeSO_4 .

II. The Ba, Cu, and Na salts of (I) are prepared. In $\text{C}_5\text{H}_5\text{N}$, (II) gives a Bz_2 derivative, m.p. 171° . When distilled with Zn in H_2 , (I) yields quinoline. Heated at 300° , (I) loses CO_2 ; the HCl extract contains the hydrochloride, m.p. $>300^\circ$, of a dihydroxyquinoline, m.p. $>300^\circ$ (Bz_2 derivative, m.p. 178°). With $\text{POCl}_3\text{-PCl}_5$, (I) gives a Cl-derivative, $\text{C}_{10}\text{H}_6\text{O}_3\text{NCl}$, m.p. $209\text{--}210^\circ$ (decomp.); with Ac_2O , (I) gives the reddish-violet colour of a 2-hydroxyquinolinecarboxylic acid. Other colour reactions of (I), in comparison with kynurenine acid (III), are described.

III. The urine from which (I) is extracted contains small amounts of (III) and of kynurenine (IV). The urine of rabbits on a fibrin diet also contains (I), (III), and (IV); that of dogs contains (III) and (IV) only. A method for obtaining increased amounts of (IV) by injecting tryptophan into rabbits is described.

E. W. W.

Quinolyl-4-pyruvic and -acetic acid. W. BORSCHÉ and L. BÜTSCHLI (Annalen, 1937, **529**, 266—273).—The side chains of the 2- are more active than those of the 4-quinolyl compounds. Et quinolyl-4-pyruvate (I) [2:4-dinitrophenylhydrazone, m.p. 179° , and its hydrochloride, m.p. $239\text{--}240^\circ$ (decomp.)] and PhCHO in presence of piperidine at 140° afford α -keto- γ -hydroxy- γ -phenyl- β -4-quinolylbutyrolactone, m.p. 227° (decomp.), whilst with $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$ in AcOH at 100° they give 4:5-diketo-2-phenyl-1-2'-naphthyl-3-4'-quinolylpyrrolidine, m.p. 180° (with a substance, decomp. 277°). (I) with the requisite diazo-compound in AcOH containing NaOAc yields the β -phenylhydrazone, m.p. 174° (decomp.), and β -p-tolylhydrazone, m.p. 172° (decomp.), of $\alpha\beta$ -diketo- β -4-quinolylpropionic acid. Et $\alpha\beta$ -diketo- β -4-quinolylpropionate β -p-tolylhydrazone has m.p. 147° . Et α -oximino- β -4-quinolylpropionate, m.p. $183\text{--}184^\circ$, is hydrolysed by alkali to the corresponding acid, m.p. 198° (decomp.), which passes at 200° into quinolyl-4-acetonitrile (II), m.p. $144\text{--}145^\circ$. With the requisite diazo-compound this gives the phenylhydrazone, m.p. 168° , and p-anisylhydrazone, m.p. 188° , of quinolyl-4-glyoxylonitrile and with $p\text{-NO-C}_6\text{H}_4\text{-NMe}_2$ in MeOH it affords the corresponding p-dimethylaminoanil, m.p. $133\text{--}135^\circ$. With PhCHO, $p\text{-OMe-C}_6\text{H}_4\text{-CHO}$, and $o\text{-OH-C}_6\text{H}_4\text{-CHO}$ (II) in presence of piperidine gives α -4-quinolylcinnamonitrile, m.p. $139\text{--}140^\circ$, p-methoxy- α -4'-quinolylcinnamonitrile, m.p. $143\text{--}144^\circ$, and 3-4'-quinolylcoumarin, m.p. 194° , whilst with isatin it affords 2-keto-3-4'-quinolylcyanomethene-2:3-dihydroindole, m.p. 278° . With EtOH-HCl at 100° (II) gives Et 4-quinolylacetate, m.p. 64° (picrate, m.p. 157° , after softening), which affords Et 4-quinolylglyoxylate phenylhydrazone, m.p. 196° , and is hydrolysed by 2N-NaOH to 4-quinolylacetic acid, m.p. 90° (much decomp.).

H. W.

Reactivity of benzylacetone in Pfizinger's reaction. G. B. CRIPPA and E. SCEVOLA (Gazzetta, 1937, **67**, 119—122).—Isatin in 50% KOH with $\text{COMe-CH}_2\text{-CH}_2\text{Ph}$ gives 2- β -phenylethylquinoline-4-carboxylic acid (A., 1927, 1200).

E. W. W.

Synthesis of 1-benzyltetrahydroisoquinoline bases. E. SPATH, F. KUFFNER, and F. KESZTLER (Ber., 1937, 70, [B], 1017—1019).—Homopiperonal and homopiperonylamine are kept in Et₂O at 15—20° for 30 min. The solution is evaporated and the residue is shaken violently with HCl (1:1) at 100° for 1 hr., whereby 6:7-3':4'-dimethylenedioxy-1-benzyl-1:2:3:4-tetrahydroisoquinoline, m.p. 84—85°, is obtained in 2.33% yield. It is further identified by conversion into 2:3-12:13-dimethylenedioxyberbine, m.p. 213—214°. The observations of Hahn and Schales (A., 1936, 618) could not be confirmed.

H. W.

Imidochlorides. V. Synthesis of hydroxycarbethoxyphenyl- α - and - β -naphthaquinolines. V. R. HEERAMANICK and R. C. SHAH (J.C.S., 1937, 867).—Et α - and β -naphthyliminobenzylmalonate are cyclised by heating to Et 4-hydroxy-2-phenyl- α -naphthaquinoline-3-carboxylate, m.p. 228—230°, and Et 1-hydroxy-3-phenyl- β -naphthaquinoline-2-carboxylate, m.p. 280—282° (acid, m.p. 248—250°; picrate, m.p. 179—181°).

F. R. S.

Medicinal products from acridine compounds.

III. Tetrahydro-derivatives. O. J. MAGIDSON and A. I. TRAVIN (J. Gen. Chem. Russ., 1937, 7, 842—852).—5-Chloroanthranilic acid and cyclohexanone (I) (150°; 90 min.) yield 7-chloro-1:2:3:4-tetrahydroacridone, m.p. 385°, which with POCl₃ (120°; 3 hr.) gives 5:7-dichloro-1:2:3:4-tetrahydroacridine, m.p. 84—85°, and this with PhOH (120°; 3 hr.) gives 7-chloro-5-phenoxy-1:2:3:4-tetrahydroacridine, m.p. 127—128°, and with PhOH and NH₂·CHMe·[CH₂]₄·NEt₂ (180°; 5 hr.) yields 7-chloro-5-(8-N-diethylamino- α -methylbutyl)amino-1:2:3:4-tetrahydroacridine, b.p. 230—240°/1 mm. (meconate, decomp. at 85—90°). 4-Chloroanthranilic acid and (I) yield 8-chloro-1:2:3:4-tetrahydroacridone, m.p. 380°, from which 5:8-dichloro-, m.p. 87—89°, 8-chloro-5-iodo-, m.p. 115—116°, and 8-chloro-5-(8-N-diethylamino- α -methylbutyl)amino-1:2:3:4-tetrahydroacridine are prepared as above. 5-Nitroanthranilic acid and (I) at 220° yield 7-nitro-1:2:3:4-tetrahydroacridone, m.p. 324—325°, identical with that obtained by nitration of 1:2:3:4-tetrahydroacridone at -15°, and from which 5-chloro-7-nitro-1:2:3:4-tetrahydroacridine, m.p. 148—149°, is obtained with POCl₃ at 125° (3 hr.). 5-Chloro-8-nitro-, m.p. 149—150°, and 8-nitro-5-(8-N-diethylamino- α -methylbutyl)amino-1:2:3:4-tetrahydroacridine (meconate, decomp. at 110—115°) are prepared analogously. 1:2:3:4-Tetrahydroacridine-5-carboxylic acid and POCl₃ (100°; 1 hr.) yield the acid chloride, m.p. 198—200° (decomp.), from which the diethylamide, m.p. 102—103° (hydrochloride, m.p. 245—246°), and β -N-diethylaminoethylamide dihydrochloride, m.p. 246—248°, and the β -N-diethylaminoethyl ester (dihydrochloride, m.p. 188—189°) are prepared.

R. T.

Acridones. X. p-Chlorophenylanthranil and 3-chloroacridone. I. TANASESCU and A. SILBERG (Bull. Soc. chim., 1936, [v], 3, 2383—2385; cf. A., 1936, 1509).—p-Aminophenylanthranil (I) (A., 1933, 275) is converted (Sandmeyer) into p-chlorophenyl-

anthranil, m.p. 152°, which with boiling H₂O, EtOH, Zn, and CaCl₂ gives 4-chloro-2'-aminobenzophenone, m.p. 120° (Bz derivative, m.p. 136°), and with NaNO₂ and conc. H₂SO₄ gives 3-chloroacridone. Attempts to convert (I) into 3-aminoacridone by this method failed.

H. G. M.

Photoluminescence spectrum of glycerol solution of tryptaflavine.—See A., I, 346.

Syntheses of isomeric ethylphenanthridines.

H. KONDO and S. UYEO (Ber., 1937, 70, [B], 1094—1097).—Treatment of o-C₆H₄Br·CHO and 1:3:2-C₆H₃EtBr·NH₂ with Cu powder at 230—240° gives 1-ethylphenanthridine, b.p. 110—140° (bath)/0.03 mm. [picrate, m.p. 231°; styphnate, m.p. 226° (decomp.); double compound with HgCl₂, m.p. 212—219°]. 3:1:4-NO₂·C₆H₃Et·NH₂ is transformed into 4-bromo-3-nitroethylbenzene, b.p. 127°/4 mm., reduced to 4-bromo-3-aminoethylbenzene, b.p. 113—115°/4.5 mm. (Ac derivative, m.p. 108—109°), which with o-C₆H₄Br·CHO and Cu powder at 240—250° gives 2-ethylphenanthridine, b.p. 110—140°/0.04 mm. (picrate, m.p. 216°; styphnate, decomp. 236°). p-C₆H₄Et·NHAc and Br in AcOH afford 3-bromo-4-acetamidoethylbenzene, m.p. 92°, hydrolysed to 3-bromo-4-aminoethylbenzene, b.p. 100—101°/3 mm., m.p. about 9°, which with o-C₆H₄Br·CHO gives 3-ethylphenanthridine, b.p. 120—130° (bath)/0.05 mm., m.p. 62—63.5° [styphnate, m.p. 252° (decomp.); picrate, m.p. 230°]. o-C₆H₄Et·NHAc is converted by conc. HNO₃ in Ac₂O·AcOH at 0° into the 3-NO₂-derivative, hydrolysed to 3-nitro-2-aminoethylbenzene, b.p. 146—149°/5 mm., m.p. 29—30.5° (hydrochloride). The base is transformed into 2-bromo-3-nitroethylbenzene and thence into 2-bromo-3-aminoethylbenzene (Ac derivative, m.p. 112°), which affords 4-ethylphenanthridine [picrate, m.p. 223° (decomp.); styphnate, m.p. 216° (decomp.)].

H. W.

New ring systems. III. Phenyl-1:2-methoxynaphthylamine o-8-ketone. W. KNAPP (Monatsh., 1937, 70, 251—258).—1-C₁₀H₇Br and o-NH₂·C₆H₄·CO₂H are converted by Cu powder and anhyd. K₂CO₃ in boiling PhNO₂ into o-1'-naphthylaminobenzoic acid (I), m.p. 207°, and o-di-1'-naphthylaminobenzoic acid, m.p. 272—274° (decomp.). (I) and P₂O₅ in boiling PhMe afford 3:4-benzaacridone, m.p. 365—366° (incipient decomp.). 1:2-C₁₀H₆Br·OMe (improved prep. from β -C₁₀H₇·OMe and Br in AcOH) similarly yields o-2'-methoxy-1'-naphthylaminobenzoic acid (II), m.p. 208—209° (sparingly sol. alkali salts), more advantageously obtained from 1:2-NH₂·C₁₀H₆·OMe and o-C₆H₄Cl·CO₂H, and o-di-2'-methoxy-1'-naphthylaminobenzoic acid, m.p. 250—251° (cryst. alkali salts). Phenyl-1:2-methoxynaphthylamine o-8-ketone (III), C₆H₄<NH>C₁₀H₅·OMe, m.p. 190—192°, is obtained from (II) and P₂O₅ in boiling PhMe. Treatment of (II) with PCl₅ gives a reddish-brown mixture, apparently unchanged by AlCl₃ and giving a product not identical with (III). When heated above its m.p. (I) gives NHPh·C₁₀H₇· α ; similarly (II) affords phenyl-2-methoxy- α -naphthylamine, m.p. 82—83°.

H. W.

Identification of phenylhydrazones and isomeric pyrazolines obtained from chalkones. L. C. RAIFORD and W. J. PETERSON (J. Org. Chem., 1937, 1, 544—552).—Chalkonephenylhydrazones on filter-paper with Br vapour give a yellow colour, changing to orange or brick-red; the isomeric pyrazolines give an immediate green colour. Differentiation is also possible by reduction and by crystal form. Hydrogenation (PtO_2) of $\text{COPh}\cdot\text{CH}\cdot\text{CHPh}$ and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$ gives $\text{COPh}\cdot\text{C}_6\text{H}_4\text{Ph}$ (phenylhydrazone, an oil) and $p\text{-chloro-}\beta\text{-phenylpropio-phenone}$, m.p. 73° (oxime, m.p. $91\text{--}92^\circ$). Na-Hg-CO_2 reduces chalkones and their phenylhydrazones to $\beta\text{-phenylpropio-phenones}$ and their phenylhydrazones, respectively, but does not affect 1:3:5-triphenylpyrazolines; Na-EtOH reduces the phenylhydrazones to NH_2Ph . The following are described: phenylhydrazones, m.p. $116\text{--}118^\circ$, $101\text{--}102^\circ$, and $106\text{--}107^\circ$, of $p\text{-bromo-}$, -methyl- (forms, m.p. 77° , $55\text{--}56^\circ$, and 44°), and -methoxy- $\beta\text{-phenylpropio-phenone}$, respectively; 1:5-diphenyl-3- $p\text{-chloro-}$, m.p. $150\text{--}150.5^\circ$, -bromo-, m.p. $156\text{--}157^\circ$, -hydroxy-, m.p. $116\text{--}118^\circ$, -methoxy-, m.p. $141\text{--}141.5^\circ$, -acetoxy-, m.p. $165\text{--}166^\circ$, - $m\text{-nitro-phenyl-}$, m.p. 131° , and -3- $p\text{-tolyl-pyrazoline}$, m.p. $152\text{--}153^\circ$. R. S. C.

Action of ethyl oxalate on pyrazolones. G. PERRONCITO (Gazzetta, 1937, 67, 158—164).—1-Phenyl-3-methylpyrazol-5-one (I) and $\text{Et}_2\text{C}_2\text{O}_4$ at 180° give bis-(1-phenyl-3-methyl-5-keto-4-pyrazolylene)-glycol Et_2 ether (II), m.p. 163° (Br_2 additive compound, m.p. 80°). $\text{Me}_2\text{C}_2\text{O}_4$ gives the Me_2 ether (III), m.p. 193° . $\text{H}_2\text{C}_2\text{O}_4$ gives methenyldi-(1-phenyl-3-methylpyrazol-5-one) (A., 1930, 1182). With boiling 20% KOH , (II) or (III) gives bis-(1-phenyl-3-methyl-5-keto-4-pyrazolyl) diketone, m.p. 137° (corresponding quinoxaline, m.p. $>300^\circ$; monophenylhydrazone). With Zn-AcOH , (II) yields bis-(1-phenyl-3-methyl-5-keto-4-pyrazolyl)glycol Et_2 ether, m.p. 208° .

E. W. W.

Derivatives of cyclotetramethylenepyrazole and their molecular compounds with substituted barbituric acids. H. RÜHKOPF (Ber., 1937, 70, [B], 939—942).—Et cyclohexan-2-onecarboxylate and $\text{NHPh}\cdot\text{NH}_2$ afford the corresponding phenylhydrazone, m.p. 98° , which passes when heated into 1-phenyl-3:4-cyclotetramethylenepyrazol-5-one, b.p. $\sim 200^\circ/12\text{ mm.}$, m.p. 180° , whence the 2-methyl (I), b.p. $220^\circ/12\text{ mm.}$, m.p. 106.5° , 2-ethyl, b.p. $\sim 250^\circ/12\text{ mm.}$, m.p. 106° , 2-benzyl, b.p. $294^\circ/40\text{ mm.}$, m.p. 82° , and 2-acetyl, b.p. $225^\circ/40\text{ mm.}$, m.p. 131° , derivatives. cycloTetramethylenepyrazolones, unsubstituted at 2, do not give mol. compounds with barbituric acids. Such compounds (1:1), m.p. 108° , 161° , and 120.5° , respectively, are given by (I) with diethyl-, dipropyl-, (II), and allylisopropyl- (III)-barbituric acid. Similar compounds (1:1), m.p. 146.5° and 140° , respectively, are obtained from 1-phenyl-2-methyl-3:4-cyclotrimethylenepyrazol-5-one and (II) or (III). H. W.

Action of hydroxylamine and hydrazine on acetylenic thioamides. D. E. WORRALL (J. Amer. Chem. Soc., 1937, 59, 933—934).— $\text{CPh}\cdot\text{CNa}$ and PhNCO in Et_2O give phenylpropiolthioanilide, decomp. $113\text{--}114^\circ$, sol. in NaOH , decomposed by heat

at 100° , by acid in EtOH , Hg salts, or Br ; in hot EtOH it gives the dimeride, $\text{CPh}\cdot\text{C}(\text{NPh})\cdot\text{S}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CS}\cdot\text{NHPh}$, sinters at about 250° , sol. in NaOH , and yields with Br a dibromide, decomp. $226\text{--}227^\circ$, and decomp. products; with NH_2OH it gives 3-anilino-5-phenylisooxazole, m.p. $142\text{--}143^\circ$ [yields 3- $p\text{-bromo-}$, m.p. 158° (gives BzOH , when oxidised), and 3-2':4'-dinitro-anilino-5-phenylisooxazole, m.p. $245\text{--}246^\circ$], and some 1-phenacylbenzthiazole, m.p. $190\text{--}191^\circ$; with $\text{NHPh}\cdot\text{NH}_2$ it gives 3-anilino-1:5-diphenylpyrazole, m.p. $153\text{--}154^\circ$ [Br_2 , m.p. 181° , and (NO_2)₃-derivative, m.p. $197\text{--}198^\circ$], and with N_2H_4 yields 3-anilino-5-phenylpyrazole, m.p. $166\text{--}167^\circ$, which affords 3-2':4':6'-tri-bromo-, decomp. $206\text{--}207^\circ$, and -nitro-anilino-5-phenylpyrazole, decomp. 266° . R. S. C.

Lactim-lactam tautomerism. I. Oxidation by perbenzoic acid of the double linking between carbon and nitrogen. M. M. BOTVINNIK and N. L. GAVRILOV. II. Oxidation of glyoxaline and its derivatives by perbenzoic acid. M. M. BOTVINNIK and M. A. PROKOFIEV (J. pr. Chem., 1937, [ii], 148, 170—190, 191—204).—I. BzO_2H (I) in CHCl_3 is a quant. reagent for the (fixed) C:N linking; the amount used is determined iodometrically. It oxidises ($\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2$)₂Ba to NH_3 , $\text{H}_2\text{C}_2\text{O}_4$, and BzOH . Histidine dihydrochloride (II), $\text{NH}\cdot\text{C}(\text{NH}_2)_2$, and trimethyloxazole are all oxidised, with decomp. NH_2Me , $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III), $\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, $\text{CO}(\text{NH}_2)_2$, ($\text{CO}\cdot\text{NH}_2$)₂, and $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ are not oxidised, nor are Abderhalden's enolised NH_2 -acid anhydrides, nor uric acid (IV), or isoleucylhydantoin (V). The K salt of (IV) and OO' -dibenzylglycine anhydride are, however, oxidised. Thus (I) does not oxidise a lactim unless displacement of equilibrium to the lactam is excluded. In presence of MgO , however, (III), (IV), and (V) are oxidised by (I). The action of (I) on $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and on $\text{CH}_2\text{Bz}\cdot\text{COMe}$ (A., 1930, 1579) is confirmed.

II. Oxidation of glyoxaline by (I) is dependent on time and on concn. of (I); the intermediate glyoxaline dioxide, $\text{C}_3\text{H}_4\text{O}_2\text{N}_2$, decomp. 135° , is isolated; $\text{CO}(\text{NH}_2)_2$, but no $\text{H}_2\text{C}_2\text{O}_4$, is formed. Glyoxaline-4:5-dicarboxylic acid is not oxidised: it even stabilises (I). The oxidation of (II) and of 2-methyl-4:5-dihydroglyoxaline by (I) is studied. E. W. W.

Synthesis of aneurin. T. HOSHINO and M. OHTA (Proc. Imp. Acad. Tokyo, 1937, 13, 101—102).—Aneurin is synthesised from 4-methyl-5-(β -hydroxyethyl)thiazole and 6-amino-2-methyl-5-chloromethylpyrimidine hydrochloride, m.p. $214\text{--}215^\circ$ (decomp.). Other compounds mentioned are 6-hydroxy-, m.p. $183\text{--}184^\circ$, and 6-amino-2-methyl-5-ethoxymethyl- [hydrochloride, m.p. 212° (decomp.)], and 6-amino-2-methyl-5-hydroxymethylpyrimidine, m.p. $195\text{--}196^\circ$ [hydrochloride, m.p. $218\text{--}219^\circ$ (decomp.)]. A. LI.

Degradation of histidine and other glyoxaline derivatives by ascorbic acid. S. EDLBACHER and A. VON SEGESSER (Biochem. Z., 1937, 290, 370—377).—A measurable but small amount of deamination occurs when a mixture of histidine (I) and ascorbic acid is oxygenated at 38° , but when to the mixture in PO_4''' buffer at p_H 7 traces of $\text{Fe}_2(\text{SO}_4)_3$

or hæmin are added and O_2 is bubbled through, 80% of (I) is decomposed and subsequent alkalisation to the phenolphthalein red colour gives one, and more strongly with excess of NaOH gives two, equivs. of N as NH_3 . Oxidative disruption of the glyoxaline ring must therefore have occurred. The reaction does not occur when N_2 replaces O_2 . When subjected to the same treatment, (I) Me ester, glyoxalyl-lactic acid, methylhistidine, histamine, hydroxymethylglyoxaline, and glyoxaline behave similarly, whilst glycine, alanine, phenylalanine, dihydroxyphenylalanine, tyrosine, valine, leucine, arginine, ornithine, aspartic and glutamic acids, proline, creatine, uric acid, allantoin, thymine, guanine, dialuric acid, and sturine give only traces of NH_3 and hypoxanthine, adenine, and carnosine give 30% and cystine and serine 25% of NH_3 . P. W. C.

Condensations of aromatic amines with formaldehyde in media containing acid. V. Substituted dihydroquinazolines from *p*-chloroaniline and *p*-bromoaniline. E. C. WAGNER and A. EISNER (J. Amer. Chem. Soc., 1937, 59, 879—883).— p - $C_6H_4Br \cdot NH_2$ and CH_2O in dil. HCl at room temp. give 6-bromo-3-*p*-bromophenyl-3:4-dihydroquinazoline (I), m.p. 205.8° (25.9%; picrate, m.p. 242°) [obtained, but not identified, by Cairncross *et al.* (A., 1936, 487)], a base, b.p. 134—135°, and small amounts of methylated products (cf. *loc. cit.*). p - $C_6H_4Cl \cdot NH_2$ yields similarly 6-chloro-3-*p*-chlorophenyl-3:4-dihydroquinazoline (II), m.p. 192° (picrate, m.p. 239°), and a base, m.p. 135°. (p - $C_6H_4Cl \cdot N \cdot CH_2$)₃, m.p. 151°, p - $C_6H_4Cl \cdot NH_2$, and p - $C_6H_4Cl \cdot NH_2 \cdot HCl$ in $PhNO_2$ at 80—90° give 4-chloro-*N*-5'-chloro-2'-amino-benzylaniline, m.p. 93° (benzylidene derivative, m.p. 139°), converted by CH_2O in KOH-EtOH into 6-chloro-3-*p*-chlorophenyl-1:2:3:4-tetrahydroquinazoline, m.p. 158°, and by 90% HCO_2H at 100° into (II). Similarly the trimeride, m.p. 168.8°, of *p*-bromo-*N*-methylbenzylaniline gives *p*-bromo-*N*-5'-bromo-2'-amino-benzylaniline, m.p. 117.6° (benzylidene derivative, m.p. 144.6°) [with a little (I)], 6-bromo-3-*p*-bromophenyl-1:2:3:4-tetrahydroquinazoline (III), m.p. 173°, and (I). Reduction of (I) and (II) could not be effected without dehalogenation. With Na-EtOH (I), (II), and (III) give 3-phenyl-1:2:3:4-tetrahydroquinazoline. M.p. are corr. R. S. C.

Pyridino-3:4-triazoles. II. O. BREMER (Annalen, 1937, 529, 288—290; cf. A., 1935, 993).—Addition of 1-butylpyridino-(3':4')-4:5-triazole methosulphate and KOH to aq. $K_2Fe(CN)_6$ at 0° gives 2'-keto-1'-methyl-1-butyl-1:2-dihydro-pyridino-(3':4')-4:5-triazole (I), m.p. 112°, converted by HNO_3 (*d* 1.4) in conc. H_2SO_4 at $\geq 5^\circ$ into the 5'-nitro-, m.p. 103°, by Br in AcOH-KOAc into the 5'-bromo-, m.p. 138°, and by PCl_5 and $POCl_3$ into the 5'-chloro-, m.p. 136°, derivative. H. W.

Hydrazine derivatives analogous to barbituric acid and uric acid. B. HEFNER and S. FAJERSZTEJN (Bull. Soc. chim., 1937, [v], 4, 854—862).—Cyanocethyldiazide is converted by 40% NaOH at room temp. into 3-imino-5-ketopyrazolidine (I), decomp.

204° after darkening at 175°, which with a large excess of boiling Ac_2O gives 3-imino-5-keto-1:4:4-triacetyl-, m.p. 190—192°, and 3-imino-5-keto-2:4:4-triacetyl-, m.p. 130°, -pyrazolidine. 3-Imino-5-keto-1:4:4-tribenzoylpyrazolidine has m.p. 185°. (I) and $PhCHO$ in boiling EtOH afford 3-imino-5-keto-4-benzylidene-pyrazolidine (+2 H_2O), m.p. 244°, which does not react with HNO_3 . 3-Imino-5-keto-4-oximinopyrazolidine, m.p. $>300^\circ$ after changing colour at 100° and darkening at 200°, is reduced by $Na_2S_2O_4$ to (impure) 3:4-diamino-5-hydroxypyrazole (II) [sulphate (III); hydrochloride; oxalate; acetate; picrate], which strongly reduces $KMnO_4$ and $NH_3 \cdot Ag_2O$. (III) and CH_2O give 3-imino-4-methyleneamino-5-ketopyrazolidine (+2 $CH_2O \cdot H_2O$). (II) and $PhNCS$ in EtOH afford 3:4-diphenylthiocarbamido-5-hydroxypyrazole (+1.5 H_2O); attempts to prepare an analogous compound from $PhNCO$ were unsuccessful owing to instability of the product. (II) is transformed by KCN into 3-imino-4-carbamido-5-ketopyrazolidine (+ H_2O), converted by heating its Na or Ba salt into 5:7-dihydroxyglyoxalino-pyrazole, $NH \begin{smallmatrix} CO \cdot C \cdot NH \\ NH \cdot C \cdot NH \end{smallmatrix} CO$. H. W.

Alloxantin series. (Miss) D. NIGHTINGALE (J. Amer. Chem. Soc., 1937, 59, 806—808).—1-Methylalloxantin, +3 H_2O , m.p. 226° (decomp.), is obtained from methylalloxan and dialuric acid or uramil. The 1'-Me isomeride, +3 H_2O , m.p. 226° (decomp.), is obtained from methyluramil and alloxan. Separate identity is believed to be established by rapid pptn. of K dialurate from the 1-Me compound and slow pptn. from its isomeride by hot KOAc; the reaction of the 1'-Me compound is considered as due to gradual oxidation of the alloxan by 1-methyldialuric acid (I), which is shown to occur in a separate experiment. Similar results are obtained with 1:3- and 1':3'-dimethylalloxantin and support the semiacetal structure of alloxantin. Benzoyldialuric acid and the substituted alloxans give benzoyl-1-methyl-, m.p. 233° (decomp.), and -1:3-dimethyl-alloxantin, decomp. 237°. Benzoylmethyldialuric acid, m.p. 185—187° (K salt, + H_2O), from (I) and $BzCl$ at 120°, does not react with alloxan. R. S. C.

Action of acetaldehyde and benzaldehyde on 5-aminotetrazole. R. STOLLÉ and K. HEINTZ (J. pr. Chem., 1937, [ii], 148, 217—220).—The reported prep. of 4-amino-1-methylmethenyl-[1:2:3:5]-tetrazole (cf. A., 1935, 1509) from 4-amino-[1:2:3:5]-tetrazole [i.e., 5-amino-1:2:3:4-tetrazole (I)] and $MeCHO$ is not confirmed. The actual product is an aldol derivative, 4- γ -hydroxybutylideneamino-1:2:3:4-tetrazole, m.p. 170° (Ag salt); (I) does not condense with $BzCHO$ at 100°, or at 150°, at which temp. it yields guanylamino-tetrazole. E. W. W.

Dipyrazolobenzenes. V. VESELY and A. MEDVEDEVA (Coll. Czech. Chem. Comm., 1937, 9, 176—184).—6:1:2:3- $NO_2 \cdot C_6H_2Me_2 \cdot NHAc$ with N_2O_3 in Ac_2O gives its *NO*-derivative, m.p. 85° (decomp.), converted in boiling C_6H_6 into 5-nitro-4-methylindazole (Noelting, A., 1904, i, 690) (*Ac* derivative, m.p. 127—127.5°), reduced ($Fe \cdot AcOH$) to the 5- NH_2 -compound, m.p. 197°, the Ac_2 derivative of which affords its 5-*NO*-derivative, m.p. 94° (decomp.), con-

verted by boiling C_6H_6 into the 1'-Ac derivative (A; R = Ac, R' = H), sinters 205—208°, not melting completely at 305°, of 4':5':2:1:4'':5'':3:4-



dipyrazolobenzene (A; R = R' = H), m.p. >320° (1':1''-Ac₂ derivative, m.p. 215°; Ag salt), obtained by hydrolysis with KOH-EtOH and also by direct decomp. of the (NO)₂-derivative of 1:2:3:6-C₆H₂Me₂(NHAc)₂. Similarly 5:1:4:2-NO₂·C₆H₂Me₂·NHAc (improved prep.) gives a NO-derivative, m.p. 92—93° (decomp.), converted into 5-nitro-6-methylindazole (*loc. cit.*), reduced to the 5-NH₂-compound, m.p. 223—224°, the Ac₂ derivative, m.p. 233—234°, of which affords a NO-derivative, converted into the 1'-Ac derivative, m.p. 275—278° (decomp.), of 5':4':1:2:5'':4'':4:5-dipyrazolobenzene, m.p. >330° (1':1''-Ac₂ derivative, m.p. 303—305°; Ag salt).

J. W. B.

Pyrrole-blacks. I, II. P. PRATESI (Gazzetta, 1937, 67, 188—199, 199—206; cf. this vol., 123).—I. β-3-Methyl-4-pyrrolylpropionic acid (I) after some months in air and light gives a black substance, oxidised (CrO₃) to methylmaleimidepropionic acid (II). With FeCl₃-Et₂O, (I) gives a black substance, oxidised to (II); with H₂O₂ in presence of Fe⁺⁺⁺, (I) forms a similar substance. 3-Methyl-4-ethylpyrrole (III) with FeCl₃ gives a substance, oxidised (CrO₃) to methylethylmaleimide. 1-Methyl-2:5-diethylpyrrole does not yield pigments.

II. With H₂O₂-Fe⁺⁺⁺, (III) gives a substance, which with CH₂N₂ yields a methylated product. The behaviour of other pyrrole derivatives towards oxidation, and towards I, is studied, and the structure of pyrrole-blacks is discussed.

E. W. W.

Accelerating action of metallic salts and organic compounds in the aniline-black condensation. E. JUSTIN-MUELLER (Bull. Soc. chim., 1936, [v], 3, 2257—2266).—The effects of CuSO₄, NH₄VO₃, HVO₃, VOCl₂, FeSO₄, FeCl₃, K₄Fe(CN)₆, and K₃Fe(CN)₆ on the oxidation (a) of guaiacum resin with H₂O₂ and with NaClO₃, and of leuco-phenolphthalein (*cf.* A., 1917, ii, 432) with H₂O₂ are recorded and compared with their effects in the aniline-black condensation (b) (*cf. lit.*). Cu and V salts promote the liberation of active O from H₂O₂ and NaClO₃ and hence accelerate the reactions (a) and (b). V salts, especially VOCl₂, also accelerate these reactions by transference of O through an intermediate oxidation product (H₄V₂O₇). *p*-C₆H₄(NH₂)₂ and aminoazobenzene act only by means of a similar transference of O through an oxidation product.

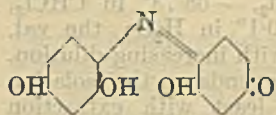
H. G. M.

Application of the cyanohydrin method to the synthesis of alkylamino-acids (hydroxyalkyl-amino-acids). A. I. KIPRIANOV and B. A. RASCHKOVAN (J. Gen. Chem. Russ., 1937, 7, 1026—1032).—NHMe·CH₂·CH₂·OH, HCl, KCN, and various aldehydes or ketones, in aq. EtOH, yield 2-phenyl-3-methyl-, 2:3-dimethyl-, and 2:2:3-trimethyl-tetrahydro-oxazole, b.p. 75—76°, with PhCHO, MeCHO, and COMe₂, respectively. NH₂·[CH₂]₃·OH·HCl similarly gives 2-phenyltetrahydro-oxazine, b.p. 175—176°/25 mm. (benzoate, m.p. 127°; picrate, m.p. 131°),

with PhCHO, and NH₂·[CH₂]₃·OH, KCN, and MeCHO yield α-(β'-hydroxyethyl)aminopropionic acid, m.p. 193°, originating from hydrolysis of the corresponding α-nitrile; it is supposed that the above oxazoles and oxazines are produced from analogous nitriles by elimination of HCN.

R. T.

Catalytic formation of resazurin. H. EICHLER (Monatsh., 1937, 70, 73—78).—Addition of aq. Na(K)NO₂ at 17—32° to *m*-C₆H₄(OH)₂·H₂O·H₂SO₄ containing MnO₂ (but not with H₂O₂, PbO₂, etc.) affords resazurin (I) (A., 1934, 1234), also formed in MeOH or EtOH solution. (I) is reduced in alkaline solution at room temp. by FeSO₄ or Na₂S₂O₄ to hydroresorufin, converted in air into resorufin (II), also obtained by reduction of (I) with NaHSO₃ or Na₂SO₃ at the b.p. Slow addition of *m*-C₆H₄(OH)₂ to NaNO₂·H₂SO₄ at <50° gives the indophenol of resorcinol (annexed formula), the postulated intermediate (Nietzki *et al.*, A., 1890, 156) in the formation of (II).



Conclusions regarding the relationship between colour, fluorescence, and constitution in this group of compounds are summarised.

J. W. B.

Hydroxydiphenyl-isatin condensation products.—See B., 1937, 530.

Manufacture of compounds of the azaphenanthrene series.—See B., 1937, 530.

Preparation of carboxylic acid amides derived from aza-compounds [-phenanthrenes].—See B., 1937, 530.

Thiazane [tetrahydrothiazine] synthesis. R. D. COGHILL (J. Amer. Chem. Soc., 1937, 69, 801—802).—Di-β-diethoxyethyl sulphide, S[CH₂·CH(OEt)₂]₂, prepared from CH₂Br·CH(OEt)₂ and K₂S or KHS, with 0.5% HCl at 40—50° gives 3:5-dihydroxythioxan, m.p. 73°, converted into the Et₂ ether by HCl-EtOH, and by HCN-NH₃ into tetrahydrothiazine-3-nitrile-5-carboxylamide, m.p. 192° (decomp.), which with hot conc. HCl gives tetrahydrothiazine-3:5-dicarboxylic acid, m.p. 253—254° (decomp.).

R. S. C.

Production of alkylaminoalkoxybenzthiazoles.—See B., 1937, 530.

Preparation of 1-thiol-5-tert.-butylbenzthiazole.—See B., 1937, 530.

Oxidation of leuco-methylene-blue by nitrates and nitrites. E. AUBEL, O. SCHWARZKOPF, and GLASER (Compt. rend. Soc. Biol., 1937, 125, 12—13).—Leuco-methylene-blue is oxidised by NO₃' in the light, and is not affected by heavy metals, whereas oxidation by NO₂' is catalysed by light and by heavy metals.

H. G. R.

Quinoline derivatives. I. T. N. GHOSH (J. Indian Chem. Soc., 1937, 14, 113—115).—*p*-Tolylthiocarbamidoacetic acid, m.p. 147—148° (decomp.), obtained from the corresponding thiohydantoin, with Ac₂O gives 2-keto-5-*p*-tolylaminodihydro-1:4-thiazole, m.p. 157—158°, which with *o*-NO₂·C₆H₄·CHO yields 2-keto-3-*o*-nitrobenzylidene-5-*p*-tolylaminodihydro-1:4-thiazole, m.p. 200—201°, reduced to 5-*p*-tolylaminothiazole-2:3(2':3')-quinoline, m.p. 191—192°. A

similar series of reactions with *p*-phenethylthiocarbamidoacetic acid, m.p. 134—135° (decomp.), affords 2-keto-5-*p*-phenethylaminodihydro-1:4-thiazole, m.p. 193—194°, 2-keto-3-*o*-nitrobenzylidene-5-*p*-phenethylaminodihydro-1:4-thiazole, m.p. 177—178°, and 5-*p*-phenethylaminothiazole-2:3(2':3')-quinoline, m.p. 175°.

F. R. S.

Accelerators for vulcanisation of rubber.—See B., 1937, 592.

Alkaloids of *Anabasis aphylla*. XII. Specific rotation of anabasine, in relation to the method of extraction from the plant, the nature of the solvent, and the concentration. S. S. NORKINA, T. NARKUZIEV, and A. P. OREKHOV (J. Gen. Chem. Russ., 1937, 7, 951—955).—Anabasine has $[\alpha]_D^{20}$ —81° with no solvent, —75.25° in COMe₂, —71.24° in C₆H₆, —71.06° in C₂H₄Cl₂, —68.78° in CHCl₃, —45.85° in EtOH, and —39.1° in H₂O; the val. of $[\alpha]_D$ in H₂O or C₆H₆ falls with increasing dilution. The val. of $[\alpha]_D$ found also depends on the isolation procedure; racemisation is least with extraction with C₂H₄Cl₂, via the silicofluoride or benzoate.

R. T.

Constitution of carpaine. III. G. BARGER, R. ROBINSON, and T. S. WORK (J.C.S., 1937, 711—713).—Carpamic acid, obtained by hydrolysis of carpaine (I) (cf. Barger, J.C.S., 1910, 97, 466), is not readily affected by K₂Cr₂O₇—H₂SO₄, giving no ketone. With P—HI, it affords a hydrocarbon, C₁₄H₂₈ (?), b.p. about 90°/high vac., similar to a hydrocarbon obtained from myristic acid. Exhaustive methylation of (I), followed by catalytic reduction, yields a lactone, hydrolysed to an acid, C₁₄H₂₈O₃, m.p. 20—25°, with one *C*-Me. Successive treatment of carpamic acid hydrochloride with PCl₅ and KOH leads to anhydrocarpamic acid, reduced (PtO₂—H₂) to deoxycarpamic acid, m.p. 181°, and oxidised with O₂ to a monobasic acid (COMe·[CH₂]₇·CO₂H?), and with KMnO₄ to agelaic and other acids. (I) is probably $\begin{array}{c} \text{CH}_2\text{CH}_2 \\ | \quad | \\ \text{CH}_2\text{NH} \end{array} > \text{CH} \cdot \text{CMc} \begin{array}{c} \text{O} \\ | \\ \text{[CH}_2\text{]}_7 \end{array} > \text{CO}$.

F. R. S.

Synthetical experiments relating to carpaine.

I. Synthesis of a basic long-chain lactone. G. BARGER, R. ROBINSON, and Y. URUSHIBARA. II. G. BARGER, R. ROBINSON, and W. F. SHORT. III. Derivatives of tetrahydrofuran and intermediates of the aliphatic series. G. BARGER, R. ROBINSON, and L. H. SMITH (J.C.S., 1937, 714—715, 715—718, 718—725).—I. γ -Keto- Δ^4 -tetradecenoic acid and HBr give μ -bromo- γ -ketotetradecoic acid, m.p. 56°, debrominated to the corresponding OH-acid, m.p. 63—64°, which is oxidised (AcOH—CrO₃) to $\gamma\gamma$ -diketotetradecoic acid, m.p. 95.5°. The Br-acid and NH₂Me afford ν -methylamino- γ -ketotetradecoic acid hydrochloride, reduced (Na—Hg) to the γ -hydroxytetradecoic acid, m.p. 153° (hydrobromide), which is tasteless in solution, but forms a bitter-tasting lactone, analogous to carpamic acid and carpaine, respectively.

II. *N*-Bromo- κ -methylaminoundecoic acid, obtained from κ -methylaminoundecoic acid (hydrochloride, m.p. 105—105.5°) and NaOBr, does not react with H₂SO₄ to form a pyrrolidine. C₄H₄N·MgBr with θ -carbethoxynonyl chloride gives Et sebacate,

$\alpha\theta$ -di-2'-pyrryloctane, m.p. 138°, and Et θ -2'-pyrrylo-nonoate (I), m.p. 28°, hydrolysed to the acid, m.p. 85—85.5°, whilst with Et sebacate, it forms *N*- θ -carbethoxynonylpyrrole, m.p. 43°, hydrolysed to sebacic acid and C₄H₄N, and converted at 300° into (I).

III. Et tetrahydrofurfurylmalonate (II), b.p. 123°/1 mm., from the bromide and Et malonate, is hydrolysed to β -tetrahydrofurylpropionic acid, of which the Et ester, b.p. 105°/11 mm., is reduced (Na—EtOH) to γ -tetrahydrofurylpropan- α -ol. The alcohol and PBr₃ give γ -tetrahydrofurylpropyl bromide (III), b.p. 100—101°/16 mm., which with (II) affords Et bistetrahydrofurfurylmalonate, b.p. 165°/0.5 mm., hydrolysed to $\beta\beta$ -bistetrahydrofurylisobutyric acid, b.p. 173°/0.35 mm., a compound structurally related to cuskhygrine. Tetrahydrofurfuryl *p*-toluenesulphonate has m.p. 38.7—39.1°. (III), KCN, and NaI give tetrahydrofurylacetonitrile, b.p. 92.4°/13 mm., hydrolysed to the acid, b.p. 144—146°/16 mm. (II) and λ -bromo-undecanyl acetate afford $\mu\mu$ -dicarboxy- ν -tetrahydrofuryltridecan- α -ol, m.p. 108—109°. An improved method of prep. of Et 2-furoylacetate is described. Et ϵ -hydroxyhexoate is converted by SOCl₂ into the -chloro-, b.p. 106°/14 mm., and by PBr₃ or HBr—H₂SO₄ into the -bromo-ester, b.p. 122—125°/12 mm., which with CH₃Ac·CO₂Et forms Et α -acetylsuberate, b.p. 154—158°/0.28 mm., hydrolysed to η -ketononoic acid, m.p. 40—41° (2:4-dinitrophenylhydrazones, m.p. 88—89°; semicarbazones, m.p. 136°; Et ester, b.p. 141—142°/11 mm., and its semicarbazones, m.p. 108°; *p*-phenylphenacyl ester, m.p. 93.5—95°) (cf. Godchet *et al.*, A., 1931, 731). Et ζ -bromoheptoate, b.p. 135°/17 mm., and CH₃Ac·CO₂Et similarly give θ -ketodecoic acid, m.p. 47.5—48.5° [semicarbazones, m.p. 115—116° (+2H₂O, m.p. 127°); *p*-phenylphenacyl ester, m.p. 68—70°] (cf. van Romburgh, A., 1912, i, 38). Et η -ketononoate and Mg *n*-amyl bromide yield a OH-ester, converted into *p*-phenylphenacyl η -hydroxy- η -methyltridecoate, m.p. 68—71°. CH₃Ac·CO₂Et and OPh·CH₂·CH₂·CH₂Br give Et di(phenoxypropyl)acetate, m.p. 61—62°, and Et γ -phenoxypropylacetate, b.p. 164°/1 mm., which with carbomethoxypropionyl chloride forms a substance, hydrolysed by KOH to Me δ -phenoxybutyl ketone, b.p. 136—137°/1 mm. (2:4-dinitrophenylhydrazones, m.p. 97—98°), and an acid reduced (Clemmensen) and esterified to Et δ -phenoxyvalerate, b.p. 115—117°/0.42 mm., and Et η -phenoxyoctoate, b.p. 135—140°/0.42 mm. (acid, m.p. 68—70°). δ -Phenoxyvaleric acid forms a chloride, b.p. 142—144°/8 mm., characterised as the anilide, m.p. 84.5—85.5°.

F. R. S.

Alkaloids of ergot.—See A., III, 267.

Preparation of lysergic acid hydrazide.—See B., 1937, 621.

Cotarnine series. VIII. Derivatives of 1-aminomethylhydrocotarnine. B. B. DEY and (Miss) P. L. KANTAM (J. Indian Chem. Soc., 1937, 14, 91—94).—Anhydrocotarninomethylamine (picrate, m.p. 200°; sulphate, m.p. 220°) is obtained, by reduction of the nitromethane, as an oil and not a solid (cf. Magidson *et al.*, A., 1935, 767), and from it are obtained benzoyl-, m.p. 125° (hydrochloride, m.p. 238—240°; picrate, m.p. 175—177°), acetyl-, m.p. 141°, *p*-nitrobenzoyl-, m.p. 138° [hydrochloride (+H₂O)],

m.p. 234°, nitrate, m.p. 190°, picrate, m.p. 138°, p-aminobenzoyl-, m.p. 185° (Ac derivative, m.p. 135°; picrate, m.p. 167°), m-nitrobenzoyl-, m.p. 95° (hydrochloride, m.p. 185°; picrate, m.p. 196—198°), m-aminobenzoyl-, m.p. 80°, o-nitrobenzoyl-, m.p. 143—145° [hydrochloride, m.p. 240° (decomp.); picrate, m.p. 165°], and o-aminobenzoyl-aminomethylhydrocotarnine (picrate, m.p. 175°), and a product $C_{17}H_{28}O_3N_2I_2 \cdot 2H_2O$, m.p. 135° (decomp.), by the action of MeI.

F. R. S.

Alkaloids of: (A) *Convolvulus pseudocanthabricus*. A. P. OREKHOV and R. A. KONOVALOVA. (B) *Arundo donax*. (C) *Cytisus caucasicus*. A. P. OREKHOV and S. S. NORKINA. (D) *Cytisus ratisbonensis*. S. S. NORKINA and A. P. OREKHOV. (E) *Genista tinctoria*. S. S. NORKINA, T. NARKUZIEV, and A. P. OREKHOV (J. Gen. Chem. Russ., 1937, 7, 646—653, 673—675, 743—746, 853—856, 906—910).—(A) Four new alkaloids, *convolvine* (I), $C_{16}H_{21}O_4N$, m.p. 115° (nitrate, m.p. 212—214°), *convolamine* (II), $C_{17}H_{23}O_4N$, m.p. 114—115° [hydrochloride, m.p. 237—239°; picrate, m.p. 263—264° (decomp.); platinochloride, m.p. 216—217°; aurichloride, m.p. 202—203°; methiodide, m.p. 273—275°], *convolvidine* (III), $C_{33}H_{42}O_8N_2$ or $C_{33}H_{44}O_8N_2$, m.p. 192—193°, and *convolvicine* (IV), $C_{10}H_{16}N_2$, b.p. 250—260° (picrate, m.p. 260—262°), have been isolated from Central Asiatic specimens of the plant. When hydrolysed with 10% KOH in MeOH (I) yields nortropine and veratric acid (V), and is identical with veratroynortropine. (II) is the N-Me derivative of (I), and is synthesised from tropine and veratroyl chloride in PhMe (at the b.p.). (II) gives (V) and an unidentified NH_2 -alcohol, m.p. 272—273°, when hydrolysed. (IV) is present in traces only, and no information as to its structure was obtained.

(B) Donaxine (A., 1935, 634, identical with von Euler's gramine, A., 1936, 741) [picrate, m.p. 144—145°; perchlorate, m.p. 181°; platinochloride, m.p. 180—181° (decomp.); methiodide, m.p. 176—177°] yields skatole when distilled from Zn; von Euler's results are thus confirmed.

(C) *d*-Lupanine (VI), pachycarpine, and an alkaloid, m.p. 120—121°, not identical with cytisine (VII) or methylcytisine (VIII) have been found in extracts of the plant.

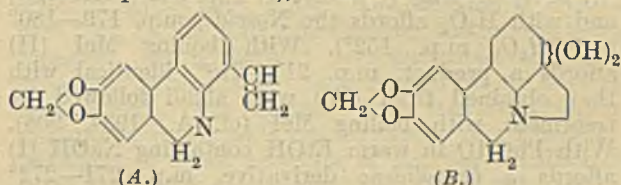
(D) The plant contains 0.16% of alkaloids, consisting of (VI), with traces of *l*-sparteine (IX) when the material is collected in May, and of (VI) 70%, and (IX) 30% in October.

(E) The plant contains 0.33% (dry wt.) of alkaloids, of which anagryne, (VII), (VIII), and an unknown alkaloid, m.p. 95—96° (picrate, m.p. 244—246°), were isolated.

R. T.

Lycoris alkaloids. X. Constitution of lycorine. H. KONDO and S. UYEO (Ber., 1937, 70, [B], 1087—1093).—2:3- $NH_2 \cdot C_6H_3Br \cdot CO_2Me$ and 6-bromopiperonal (I) are converted by Cu powder at 200° into Me 6:7-methylenedioxyphenanthridine-1-carboxylate, m.p. 149—151°, which could not be caused to react with MeI or Me_2SO_4 and therefore could not be transformed into the corresponding N-methylphenanthridone (A., 1935, 1387). Lycorine-anhydromethine (II) (*loc. cit.*) is hydrogenated to

dihydrolycorineanhydromethene, m.p. 87.5° [picrate, m.p. 174° (decomp.); methiodide, m.p. 236° (decomp.) after softening at about 225°], which when distilled with Zn dust gives 1-methylphenanthridine, phenanthridine, and 6:7-methylenedioxy-1-ethylphenanthridine (III), m.p. 142° [picrate, m.p. 257° (decomp.)]. The constitutions A and B are therefore assigned to (II) and lycorine, respectively. 2:3- $(NO_2)_2C_6H_3Et$ with $SnCl_2 \cdot HCl \cdot EtOH$ at 0—2° gives 2-nitro-3-aminoethylbenzene, m.p. 32—33° (Ac derivative, m.p. 114—115°), which is converted into



3-bromo-2-nitroethylbenzene, b.p. 113°/3 mm., whence 3-bromo-2-aminoethylbenzene (IV), b.p. 115°/7 mm. (Ac derivative, m.p. 122°, oxidised to 3-bromo-2-acetamidobenzoic acid, m.p. 212°). Treatment of (IV) with (I) and Cu powder at 210—220° affords (III).

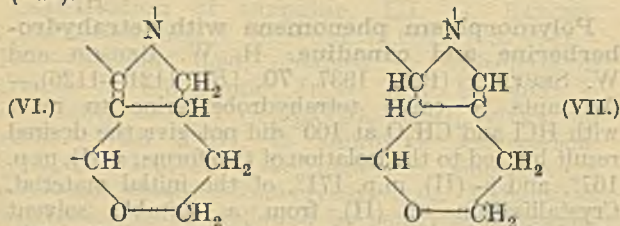
H. W.

Polymorphism phenomena with tetrahydroberberine and canadine. H. W. BERSCH and W. SEUFERT (Ber., 1937, 70, [B], 1121—1126).—Attempts to cause tetrahydroberberine to react with HCl and CH_2O at 100° did not give the desired result but led to the isolation of two forms, α - (I), m.p. 167°, and β - (II), m.p. 171°, of the initial material. Crystallisation of (II) from a suitable solvent gives (I), whereby, however, mixtures distinguishable under a lens are frequently observed. When melted and allowed to re-solidify, preferably in a high vac., (I) passes into (II). Failure in the catalytic reduction of berberine salts by previous authors is attributed largely to the use of sparingly sol. materials. This difficulty is overcome by conversion of these salts through the CM_2 derivatives into the freely sol. acetates which are readily hydrogenated (PtO_2); the differing methods of reduction do not appear to affect the relative proportions of (I) and (II) formed. The possibility of a diastereoisomeric relationship between (I) and (II) is not supported by their similar behaviour towards bromocamphorsulphonic acid, but the evidence is not conclusive by reason of the ready isomerisation of (I) and (II). Also the methobromide, m.p. 250—252°, from liquid MeBr and (I) is identical with that derived from (II). α -l-Canadine, m.p. 133°, $[\alpha]_D^{20} -297.1^\circ$ in $CHCl_3$, passes when melted and allowed to cool in a high vac. into β -l-canadine, m.p. 142°, $[\alpha]_D^{20} -298.2^\circ$ in $CHCl_3$, which is too unstable to permit recrystallisation. α - and β -l-Canadine methobromide have $[\alpha]_{5461} +145.6^\circ$ and $+145.1^\circ$ in $CHCl_3$, respectively. The evidence in favour of isomerism due to asymmetric N is therefore negative and the forms are hence regarded provisionally as polymorphous.

H. W.

Constitution of strychnine. V. Neostrychnine. M. KOTAKE and M. YOKOYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 31, 321—332).—Strychnine or methylstrychnine with Se at 250—260° affords neostrychnine (I), m.p. 226—228° (hydro-

chloride), identical with the product obtained by Robinson *et al.* (A., 1932, 527). Tafel's base (II) gives no (I) under the same conditions. With Me_2SO_4 in warm MeOH (I) affords the *methosulphate* (III), m.p. 242—243°, converted by aq. NaI into the *methiodide* (IV), decomp. 315° [also obtained from (I) or (II) with boiling MeI—MeOH], which with $\text{AgCl-H}_2\text{O}$ gives the *methochloride*, n.p. 267—268°; (III) with hot aq. NaBr similarly affords the *methobromide*, m.p. 312°. With hot CH_2PhCl (I) affords the *benzylochloride* [$+0.5\text{EtOH}$, m.p. 235° (decomp.)] and with H_2O_2 affords the *N-oxide*, m.p. 179—180° ($+3.5\text{H}_2\text{O}$, m.p. 152°). With boiling MeI (II) affords a product, m.p. 217—218°, identical with that obtained from (IV) with alkali followed by treatment with boiling MeI (cf. A., 1934, 908). With PhCHO in warm EtOH containing NaOH (I) affords a *benzylidene* derivative, m.p. 271—272° (Robinson's has m.p. 158—159°). The hydrochloride of (I) loses its HCl in vac. [strychnine (V) hydrochloride does not], which indicates that (IV) is less basic than (V). It is suggested that the double linking in (V) has shifted into either of the positions shown in (VI) or (VII).



With KMnO_4 in COMe_2 at 10° (I) affords *diketone-strychnine*, m.p. 234—235° [*mono-p-nitrophenyl-hydrazone*, m.p. 269—270° (decomp.); *monoxime* $+1.5\text{H}_2\text{O}$, m.p. 317—318° (decomp.); *monobenzyldene* derivative $+1\text{H}_2\text{O}$ (VIII), m.p. 307—308° (decomp.)], which with conc. HCl affords a *hydrochloride*, decomp. 315°, converted by $\text{AuCl}_3\text{-EtOH}$ into an *aurichloride*, m.p. 201—203°. 6N-HCl dissolves (I), and an oil, sol. in hot H_2O , is pptd. by NaOH, which indicates that (I) is probably altered by acid. With KMnO_4 in COMe_2 at 29° (VIII) affords *dihydroxy-benzylideneneostrychnine*, m.p. 229°; the benzylidene derivative of (V) under similar conditions affords a $(\text{OEt})_4$ -compound, decomp. 231°. With Ag_2O in warm MeOH (IV) gives *de-N-methylneostrychnine*, m.p. 227—229°.

J. L. D.

Constitution of strychnine. VII. Absorption spectra of strychnine and its derivatives. M. KOTAKE, K. MORI, and T. MITSUWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 31, 333—334).—Indole, indolylethylamine, and yohimbine have analogous absorption spectra, but different from that of strychnine (I). (I), dihydro- and neo-strychnine, strychninonic acid, Tafel's base, β - and α -strychninolone, and α -dihydrostrychninolone have the same absorption spectra as acylcarbazolines and probably contain the same skeleton.

J. L. D.

Synthesis of domesticin ethyl ethers. H. SHISHIDO (Bull. Chem. Soc. Japan, 1937, 12, 150—154).—3:4-Methylenedioxyphenylacetic acid with 3-methoxy-4-ethoxy- β -phenylethylamine at 180—190°

affords 3:4-methylenedioxyphenylacet- β -(3'-methoxy-4'-ethoxyphenyl)ethylamide, m.p. 114—115°, which with POCl_3 in PhMe at 130—140° followed by treatment with MeI gives 6-methoxy-7-ethoxy-1-piperonyl-N-methyl-dihydroisquinoline, m.p. 145°, reduced ($\text{Zn-H}_2\text{SO}_4$) to the corresponding H_5 -compound (I), m.p. 105—106°. (I) with conc. $\text{HNO}_3\text{-AcOH}$ below 5° affords 6'-nitro-6-methoxy-7-ethoxy-1-piperonyl-N-methyltetrahydroisquinoline, m.p. 178—179°, reduced ($\text{SnCl}_2\text{-HCl}$) to the 6'- NH_2 -compound, m.p. 96—98° [*monohydrochloride*, m.p. 228° (decomp.)], the diazonium derivative of which when boiled with Cu affords a product, reduced (Zn-HCl) to dl-2:3-methylenedioxy-6-methoxy-5-ethoxy-N-methylaporphin, m.p. 132° [*hydrochloride*, m.p. 275—277° (decomp.)], resolved with *d*-tartaric acid into the *l*-base, m.p. 129—131°, [α] $_D^{25}$ -110.9° in MeOH [*d*-tartrate, m.p. 237° (decomp.); *hydrochloride*, m.p. 257° (decomp.)], and with *l*-tartaric acid into the *d*-base, m.p. 131°, [α] $_D^{25}$ +110.8° in MeOH [*l*-tartrate, m.p. 237° (decomp.); *hydrochloride*, m.p. 257° (decomp.)], identical with domesticin Et ether.

J. L. D.

Diarsyls. IX. Tetra-3-amino-4-hydroxy-phenyldiarsyl. F. F. BLIOKE, J. F. ONETO, and G. L. WEBSTER (J. Amer. Chem. Soc., 1937, 59, 925—927; cf. this vol., 267).—Di-*p*-hydroxyphenylarsinic acid, m.p. 246—247° (decomp.), with Br-AcOH gives $\text{C}_6\text{H}_4\text{Br}_2\text{-OH}$ and with HI-AcOH gives quantitatively AsI_3 . Di-3-nitro-4-hydroxyphenylarsinic acid yields, by standard methods, di-3-nitro-4-hydroxyphenyl-chloro-, m.p. 142—143°, and -bromoarsine, m.p. 131—132°, by Fe(OH)_2 di-3-amino-4-hydroxyphenylarsinic acid, decomp. 218° (darkens at 210°), and -chloroarsine dihydrochloride, tetra-3-amino-4-hydroxyphenyldiarsyl oxide, m.p. 152—155° (decomp.), and thence (H_3PO_3) tetra-3-amino-4-hydroxyphenyldiarsyl, m.p. 193—194°, stable when solid, unstable in alkaline solution [tetrahyppophosphite, m.p. 202° (decomp. from 200°); dihydrochloride (I), m.p. 170—172°]. Di-*p*-anisylbromoarsine yields tetra-*p*-anisylarsine dihydrochloride, m.p. 132—134°, and with KMnO_4 or H_2O_2 gives di-*p*-anisylarsinic acid, m.p. 190—191°, converted into the 3:3'-(NO_2) $_2$, m.p. 231° (decomp.; softens at 220°), and -(NH_2) $_2$ -acid, m.p. 183—184° (decomp.). Of these and other diphenylarsine derivatives only (I) is curative against *T. equiperdum* in white rats.

R. S. C.

Preparation of arylmercuric nitrates.—See B., 1937, 520.

Reversible splitting of organomercuric cyanides with hydrogen chloride. E. CARR (Iowa State Coll. J. Sci., 1935, 10, 61—63).—Mainly theoretical. The stability of the C-Hg linking in a series of compounds is estimated by thermal decomp. and by irreversible fission with HCl.

CH. ABS. (r)

Structure of organo-magnesium complexes. V. V. TSCHELINCEV (Compt. rend. Acad. Sci. U.R.S.S., 1937, 14, 337—340).—The structure $\text{RMg}\cdots\text{Et}_2\text{O}\cdots\text{I}$ (heat of formation 6.6 kg.-cal. when $\text{R} = \text{Et}$) rather than $\text{R}\cdots\text{Et}_2\text{O}\cdots\text{MgI}$ is preferred for Grignard etherates for the following reasons: (1) complete analogy with the complexes of MgI_2 , (2) Et_2O remains in the complex when it is converted into $\text{OR}\cdots\text{Mg}\cdots\text{Et}_2\text{O}\cdots\text{I}$, (3) Et_2O

and ROH are incorporated only between Mg and I and not between Mg and OR; thus MgI_2 forms complexes with 6, 4, and 2 EtOH, whereas $OR \cdot MgI$ forms complexes with 3, 2, and 1 EtOH, e.g., $OR \cdot MgI \cdot 3EtOH$ (-29.7 kg.-cal.). $OR \cdot MgI \cdot 2C_{10}H_7 \cdot OH$ (-12.1), and $OR \cdot MgI \cdot o-C_6H_4Me \cdot OH$ (-4.7). Structural formulæ are suggested.

J. W. B.

Acylseleno-ureas [-carbamides]. I. B. DOUGLASS (J. Amer. Chem. Soc., 1937, 59, 740—742).—Acyl chlorides and $KSeCN$ in $COMe_2$ give solutions which are shown to contain much *acylisoselenocarbimide* by reaction with amines to give selenocarbamides. The following are described: *benzoyl*-, m.p. 194—195°, *N-benzoyl-N'-phenyl*- (I), m.p. 144—145°, *-N'-o-*, m.p. 124—125°, and *-p-tolyl*-, m.p. 154—155°, *-N'-β-naphthyl*-, m.p. 171—172°, *-N'-benzyl*-, m.p. 115—116°, and *-N'N'-diethyl*-, m.p. 110°, *N-acetyl-N'-phenyl*-, m.p. 184—185°, and *N-pyromucyl-N'-phenyl-selenocarbamide*, m.p. 106—107°. M.p. are corr. Yields are variable. $AgNO_3$ in EtOH converts (I) into $NHPh \cdot CO \cdot NHBz$.

R. S. C.

Selenium derivatives of salicylic acid. R. E. NELSON and G. S. BOASE (Proc. Indiana Acad. Sci., 1934, 44, 135—137).—Bromination of 5:5'-selenodisalicylic acid (I) yields 3:5-dibromosalicylic acid, m.p. 223°. Me_2 5:5'-selenodisalicylate selenodichloride (II) with Me salicylate and $AlCl_3$ affords Me_2 5:5'-selenodisalicylate (III), m.p. 158°, converted into the *selenodibromide*, m.p. 143°, by Br ; with Me_2SO_4 (III) gives (I). With aq. $NaCN$ (II) affords 5:5'-selenodisalicylate *selenodihydroxide*, m.p. 137°.

CH. ABS. (r)

Physicochemical studies of organometallic and furan compounds. W. E. CATLIN (Iowa State Coll. J. Sci., 1935, 10, 65—67).—Vals. are given for the relative reactivities of various halogenated furyl derivatives. Halogens attached to the furan ring are inert. The parachors of certain furan derivatives were measured. Data are given for the ionisation consts. of furan acids. The relative reactivities of organometallic compounds were measured by adding them in excess to an acid, and following the reaction by extracting the unchanged acid with H_2O . Using $CCl_3 \cdot CO_2H$ at 25°, relative reactivities were: $PbEt_4$ 6, $PbPh_4$ 56, $HgPh_2$ 57, $BiPh_3$ 40, $PbPh_3Et$ 2000. With HCl (25°) vals. were $SnEt_4$ 6.9 and (at 10°) $PbEt_4$ 410, $SnPh_4$ 75, $HgEt_2$ 30. Diatomaceous earth and O_2 (or oxidation products) catalysed the reactions.

CH. ABS. (e)

Preparation of proteins by ultracentrifuging.—See A., III, 253.

Use of refractometry in organic analysis. M. M. SAMIGIN (J. Phys. Chem. Russ., 1936, 8, 839—844).—Knowledge of d and n of a compound is sometimes sufficient for determining its type. J. J. B.

Quantitative macro- and micro-determination of sulphur in organic compounds. A. SCHÖBERL (Angew. Chem., 1937, 50, 334—337).—The material is burnt in air or O_2 in a SiO_2 tube, the combustion being localised and prevented from striking back by the insertion of fritted quartz discs. SO_3 + any SO_2 is adsorbed in H_2O_2 . SO_4^{2-} is determined by pptn. with benzidine. J. S. A.

Determination of sulphur and chlorine in combustible materials. H. KREKELER (Angew. Chem., 1937, 50, 337; cf. preceding abstract).—The method is applicable to the determination of halogens, alkaline $Na_2S_2O_3$ being used as absorbent. 0.01% of Cl in combustible gases may be so determined.

J. S. A.

Determination of arsenic and antimony in organic compounds and mixtures. E. SCHULEK and R. WOLSTADT (Z. anal. Chem., 1937, 108, 400—406).—Org. material is destroyed by heating with conc. H_2SO_4 + 30% H_2O_2 . The solution is treated with 20% HCl + KBr , and distilled, the process being repeated. As is distilled over quantitatively, Sb^{III} remaining in the flask. Both As and Sb are titrated with $KBrO_3$. For titration with 0.01N- $KBrO_3$, α -naphthoflavone is added as indicator. For the determination of small amounts of As, the distillate is freed from HCl by evaporation with H_2SO_4 + 30% H_2O_2 . As is then reduced with N_2H_4 , H_2SO_4 before titration with $KBrO_3$.

J. S. A.

Destruction of organic mercury compounds for the determination of this element. C. V. BORDEIANU (Ann. Sci. Univ. Jassy, 1935, 20, 129—131).—The organo-Hg compound (0.3—0.5 g.) mixed with finely powdered $KMnO_4$ (1—1.5 g.) is treated dropwise with cold fuming HNO_3 (10 c.c.), then with conc. H_2SO_4 (1—2 c.c.), and the mixture is heated at 100°. After dilution (50 c.c.) the excess of $KMnO_4$ is destroyed by 3% H_2O_2 and the Hg is determined by thiocyanate. The error is very small.

J. W. B.

Determination of chromium in organic compounds. C. F. MILLER (Chem. Analyst, 1936, 25, No. 1, 5—6).—Wet digestion of a 10-g. sample with conc. H_2SO_4 and HNO_3 is recommended. The solution is made alkaline and oxidised with Na_2O_2 . The Cr is determined iodometrically or colorimetrically with diphenylsemicarbazide.

CH. ABS. (e)

Micro-determination of hydroxyl and amino-groups. F. H. STODOLA (Mikrochem., 1937, 180—183).—The material is acetylated at 95—100° with a weighed quantity of a standard $Ac_2O-C_5H_5N$ mixture. The excess of Ac_2O is then titrated back with CO_2 -free $NaOH-EtOH$.

J. S. A.

Determination of fumaric acid in protein solutions containing succinic acid. E. STOTZ (J. Biol. Chem., 1937, 118, 471—477).—Fumaric acid (I) is pptd. as Hg^I salt in presence of 5% HNO_3 and the Hg^I oxidised to Hg^{II} which is then titrated with standard $KCNs$. 2—12 mg. of (I) can be determined in presence of proteins and succinic and malic acids.

J. N. A.

Spectrophotometric studies of colour development in the analysis of sugar by the Benedict method and of cholesterol by the Liebermann-Burchard reaction. F. W. SUNDERMAN and J. RAZEK (J. Biol. Chem., 1937, 118, 397—404).—The development of colour in the two above reactions is studied by means of a photo-electric spectrophotometer which recorded within 10 sec. the transmission at each λ throughout the visible range, the first curve being obtained 2 min. after prep. of the solution and

subsequent curves at intervals up to 1 hr. The optimal spectral zone is selected.

P. W. C.

Microscopic tests for amino-acids. J. D. SURMATHIS and M. L. WILLARD (Mikrochem., 1937, 21, 167—170).—The reactions of the usual alkaloid reagents and of heavy-metal salts with glycine (I), cystine (II), tyrosine (III), alanine, leucine, glutamic acid, aspartic acid, phenylalanine, and proline are described. For (I), (II), and (III) the crystal habits of the ppts. obtained serve as sp. tests. J. S. A.

Microscopy of amino-acids and their compounds. III. Copper salts. B. CUNNINGHAM, M. MACINTYRE, and P. L. KIRK (Mikrochem., 1937, 21, 245—249).—Characteristic crystal habits and optical data are described for the Cu salts of alanine, aspartic acid, cystine, glycine, isoleucine, leucine, lysine, methionine, norleucine, norvaline, phenylalanine, serine, and α -amino-*n*-valeric acid. J. S. A.

Inhibitors of colour development in the Sullivan method for cystine.—See A., III, 288.

***p*-Aminobenzenesulphonamide and its determination.** E. SCHULEK and I. BOLDIZSAR (Z. anal. Chem., 1937, 108, 396—400).—*p*-Aminobenzenesulphonamide (I), m.p. 165° (corr.), may be determined bromatometrically by addition of a 10—30% excess of 0.1*N*-KBrO₃ to a solution of the material in HCl. KBr + HCl are added, using a stoppered reaction vessel. KI is then added, and the I liberated is titrated with Na₂S₂O₃. Alternatively, (I) is hydrolysed by refluxing with 70% H₂SO₄, whereby NH₃ is split off quantitatively. The liquid is then made alkaline, and NH₃ is distilled into 0.1*N*-acid.

J. S. A.

Colorimetric determination of the components of 3:4-dihydroxyphenylalanine-tyrosine mixtures. L. E. ARNOW (J. Biol. Chem., 1937, 118, 531—537).—3:4-Dihydroxyphenylalanine (I) is determined colorimetrically against a standard of (I), or, using a green Wratten 61 filter, of pyrocatechol, by the colour produced on adding HCl, NaNO₂-Na₂MoO₄ (giving yellow), followed by NaOH (giving red). Tyrosine is determined by adding HgSO₄-H₂SO₄, heating at 100°, adding NaNO₂, centrifuging if (I) is present, and comparing the yellow colour against a standard.

E. W. W.

Microchemical detection of di- and tri-hydric phenols by drop reactions. J. KISSER and Y. KONDO (Mikrochem., Molisch Festschr., 1936, 259—270).—Characteristic sensitive colour reactions of *o*-, *m*-, and *p*-C₆H₄(OH)₂, 1:3:5- and 1:2:3-C₆H₃(OH)₃ with FeCl₃, Ti₂(SO₄)₃, (NH₄)₂Ce(NO₃)₆, *p*-Ph-N₂-C₆H₄-SO₃H, fast red salt B, and AgNO₃ + NH₃ are described.

J. S. A.

Identification of isomeric piperic acids by microchemical methods. H. LOHAUS and M. STEINER (Mikrochem., 1937, 21, 159—166).—The characteristic crystal habits and optical characteristics of piperic, isopiperic, isochavicic, and γ -bromoisochavicic acids, and of Me γ -bromoisochavicic are described.

J. S. A.

Bromatometric determination of 8-hydroxyquinoline. Determination of 8-hydroxyquinoline in pharmaceutical preparations. E. SCHULEK and O. CLAUDE (Z. anal. Chem., 1937, 108, 385—396).—Sufficient material to contain 20—40 mg. of 8-hydroxyquinoline (I) is dissolved in HCl, and the solution is made just alkaline. KBr, a 10—30% excess of 0.1*N*-KBrO₃, and HCl are added, a stoppered reaction vessel being used. After keeping for 5 min. in the dark, KI is added, and the I liberated is titrated with Na₂S₂O₃. (I) may be isolated from pharmaceutical preps. by distillation in steam from a solution of *p*_H 8. Alternatively, (I) may be extracted with CS₂, CHCl₃, etc. from neutral solutions, or accompanying org. materials may be extracted by utilising the amphoteric properties of (I).

J. S. A.

Microchemistry of methylxanthides. (Caffeine, theobromine, theophylline.) G. DENIGES (Mikrochem., Molisch Festschr., 1936, 52—58).—Caffeine (I), theobromine (II), and theophylline (III) give ppts. of characteristic habit with NaOBr + HCl. Characteristic crystals are also obtained by evaporating solutions of (I) in HCl, (II) in CHCl₃, and (III) in COMe₂.

J. S. A.

Micro-analysis of nitrogen in certain pyrimidines by the Dumas method. D. F. HAYMAN and S. ADLER (Ind. Eng. Chem. [Anal.], 1937, 9, 197).—The low vals. of N given for certain pyrimidines by the Pregl micro-Dumas method are corr. by mixing the substance with Cu acetate and CuO and heating to a high temp.

A. LI.

Microchemical differentiation of alkaloids on basis of the m.p. of their picrates, picrolonates, and styphnates. L. KOFLER and F. A. MÜLLER (Mikrochem., 1937, 22, 43—77).—Data are given as to the appearance, solubility, and m.p. of the ppts. obtained with aconitine, apomorphine, arceoline, atropine, berberine, brucine, quinine, quinidine, cinchonine, cinchonidine, cocaine, codeine, cotarnine, coniine, duboisine, emetine, ephedrine, ephetonine, heroine, homatropine, hydrastine, hydrastinine, lyoscyamine, lobeline, lupinine, mescaline, morphine, narceine, narcotine, nicotine, papaverine, paracodeine, pelletierine, physostigmine, pilocarpine, scopolamine, sparteine, strychnine, thebaine, theobromine, tropacocaine, veratrine, and yohimbine. Colechicine, caffeine, and theophylline give no ppts. with the reagents.

J. S. A.

Reaction for distinguishing between anabasine sulphate and nicotine sulphate. S. A. KATZ (Z. anal. Chem., 1937, 108, 408).—The Roussin Et₂O-I reagent deposits a periodide from solutions of nicotine only.

J. S. A.

Comparative microscopic tests of anabasine and related compounds; its purification and some physical constants. M. E. ZERBEY, M. T. ORINICK, and M. L. WILLARD (Mikrochem., 1937, 21, 171—179).—Reactions of non-homogeneous distillation samples of anabasine with alkaloid reagents are described. *n*, *d*, and [α]_D²⁵ for the impure material are recorded.

J. S. A.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

AUGUST, 1937.

Molecular asymmetry. H. HILLEMANN (Angew. Chem., 1937, 50, 435—447).—A discussion of mol. asymmetry of allenes and spirans, steric asymmetry, racemisation, and the effect thereon of condensed ring systems, asymmetric synthesis and the Walden inversion, polyphenyl systems and combinations with heterocyclic rings, and open-chain compounds.

H. W.

Mesomerism. I. How does the conception of mesomeric structure arise? II. Attempt to represent in a conventional way electronic linkings and unions between linkings. A. CORNILLON (Bull. Soc. chim., 1937, [v], 4, 1045—1052, 1053—1064).—I. A discussion of the mechanism of mesomeric change.

II. Theoretical.

J. L. D.

Oxidation of organic compounds with atmospheric oxygen. A. RIECHE (Angew. Chem., 1937, 50, 520—524).—Recent work on the oxidation of aldehydes, ketones, olefines, fatty acids, hydrocarbons, and ethers by atm. O_2 is summarised and the importance of the intermediate peroxide and per-acid formation is pointed out. The O frequently enters between C and H atoms, rather than attacking a double linking.

J. W. S.

Combustion of paraffin hydrocarbons.—See A., I, 416.

Ethane pyrolysis in the presence of steam. D. S. CRYDER and D. J. PORTER (Ind. Eng. Chem., 1937, 29, 667—673).—Various steam- C_2H_6 mixtures were passed through a SiO_2 tube at different temp. and, at each temp., data were obtained for the decomp. of the gaseous mixtures with the tube empty, with a SiO_2 gel catalyst, and with SiO_2 gel catalyst impregnated with Ni. Interaction of steam and C_2H_6 in the presence of Ni commenced at 430° , and practically complete decomp. of the C_2H_6 was obtained at 500° ; the corresponding temp. in both the blank and SiO_2 gel runs were 600° and 800° , respectively. In the absence of Ni, C_2H_4 formation commenced at 500 — 600° , increased rapidly to a max. at 700° , and then gave place at higher temp. to CH_4 formation which reached a max. at 1000° . In the Ni runs, C_2H_4 was found only at 800° and then in small concn. which decreased with increasing steam concn. The production of H_2 increased with temp. and the steam : C_2H_6 ratio, in both the presence and absence of Ni. In the absence of Ni, CO_2 production, though small, increased steadily with temp. whereas in the Ni runs there was an indicated max. CO_2 production at 450° and then a steady decrease with temp. CO formation increased uniformly with temp. in all the experiments.

These results indicate that CO is a primary and CO_2 a secondary product of the interaction of steam and C_2H_6 .

H. C. M.

Thermal decomposition of ethane, ethylene, acetaldehyde, etc.—See A., I, 366.

Thermal decomposition of propane-propylene-hydrogen equilibrium mixtures.—See A., I, 366.

Activation of specific linkings in complex molecules at catalytic surfaces. III. Carbon-hydrogen and carbon-carbon linkings in propane and ethylene.—See A., I, 418.

Synthesis of large molecules. H. MARK (Proc. Roy. Inst., 1937, 29, 683—694).—A lecture.

Reaction between sulphur dioxide and olefines and acetylenes. VI. Ascaridole as a catalyst for the reaction. L. L. RYDEN, F. T. GLAVIS, and C. S. MARVEL (J. Amer. Chem. Soc., 1937, 59, 1014—1015; cf. this vol., 226).—Ascaridole is a better catalyst than paraldehyde containing peroxides for the addition of SO_2 to acetylenes and Δ^a -ethylenes and causes addition to ethylenic CO_2H -, CN -, and CO_2Et -compounds, and to phenols. No known catalyst causes addition to tri- or tetra-substituted ethylenes or to acetylenes, $CR:CR$ or $CHR_2:C:CH$. Polymeric SO_2 -additive compounds are reported from *o*-allyl-anisole, m.p. 150 — 106° , and -phenol, m.p. 120 — 160° , *p*-bromallylbenzene, m.p. 255° , allyl-acetic acid, m.p. 180 — 230° , allyl cyanide, m.p. 222° , undecenoic acid, m.p. 255 — 275° , Me undecenoate, cyclohexylpropinene, m.p. 110 — 145° , and Δ^a -pentadecene (I), m.p. 120 — 140° . $C_{12}H_{25}MgBr$ and $CH_2:CBBr-CH_2Br$ give β -bromo- Δ^a -pentadecene, b.p. 145 — $155/3$ — 4 mm., converted by $NaNH_2$ in liquid NH_3 into (I), b.p. 112 — 113° (Hg derivative, $C_{30}H_{56}Hg$, m.p. 93°).

R. S. C.

(A) Hydro- and dehydro-polymerisation of ethylenic hydrocarbons. S. S. NAMETKIN, L. N. ABAKUMOVSKAJA, and M. G. RUDENKO. (B) Transformations of unsaturated hydrocarbons under the influence of aluminium chloride. S. S. NAMETKIN and M. G. RUDENKO (J. Gen. Chem. Russ., 1937, 7, 759—762, 763—775).—(A) The reaction between H_2SO_4 and butenes is represented as $BuHSO_4 + C_4H_8 \rightarrow H_2SO_4 + C_8H_{18}$; $BuHSO_4 + C_8H_{16} \rightarrow C_4H_7HSO_4$ (I) + C_8H_{18} ; $n(I) \rightarrow nH_2SO_4 + (C_4H_8)_n$.

(B) Complex mixtures of polymerides, dehydro- and hydro-polymerides of amylene, octene, or cyclohexene (II) are obtained by heating the hydrocarbons with $AlCl_3$ at 60 — 90° . In the case of (II) the pro-

ducts contain mono-, di-, and tri-*cyclohexylcyclohexane*, a pentameride of (II), and *cyclohexyltetrahydrobenzene*. It is concluded that the process of hydro-dehydro-polymerisation is of general application.

R. T.

Equilibrium dehydrogenation of *n*-butylenes to butadiene.—See A., I, 411.

Thermal reactions of unsaturated hydrocarbons. II. Kinetics and mechanism of thermal reactions of Δ^2 -butene. V. G. MOOR, A. V. FROST, and L. V. SCHILAEVA. **III. Thermal transformation of propene.** V. G. MOOR, N. V. STRIGALEVA, and A. V. FROST (J. Gen. Chem. Russ., 1937, 7, 818—831, 860—868).—II. The products given by $(\text{CHMe})_2$ at 575—600°/1 atm. are CH_4 , C_3H_6 , and C_8H_{14} ; at 600—700° the yield of gaseous products (CH_4 , H_2 , C_2H_4 , C_2H_6) and of $(\text{CH}_2\cdot\text{CH})_2$ rises. The reaction is not uni- or bi-mol. Possible intermediate reactions are discussed.

III. The reaction at 610—726°/1 atm. is represented as $3\text{C}_3\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 + \text{C}_6\text{H}_{10}$. The velocity of reaction cannot be represented by any simple equations.

R. T.

Structure of the trimeride of ψ -butylene. S. M. ORLOV (J. Gen. Chem. Russ., 1937, 7, 923—927).—Ozonisation at -20° leads to production of a mixture of acids with 1, 2, 3, 4, 5, 7, and 9 C. It is concluded that the trimeride is a mixture of $(\text{CHMeEt}\cdot\text{CMe})_3$ and $\text{CHMe}\cdot\text{CMe}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHMeEt}$.

R. T.

Polymerisation of divinyl by sodium in presence of isobutylene. V. N. LVOV (J. Gen. Chem. Russ., 1937, 7, 928—946).—A series of polymerides, $(\text{C}_4\text{H}_8)_{n-1}\cdot\text{C}_4\text{H}_8$, where n is the no. of C_4 groups and of double linkings in the mol., is obtained from $\text{CMe}_2\cdot\text{CH}_2$ (I) and $(\text{CH}_2\cdot\text{CH})_2$ (II) in presence of Na at 25°. The yield of polymerides and their content of low b.p. fractions rise with the (II) content of the original mixture. The dimeride is shown by identification of the ozonation products to be β -methyl- $\Delta^{\alpha\alpha}$ -heptadiene. The η of C_6H_6 solutions of the higher polymerides varies with their mol. wt. in accordance with Staudinger's formula. The isomerides in which $n = 3$, b.p. 85—87°/19 mm., $n = 4$, b.p. 70—80°/0.15 mm., $n = 5$, b.p. 95—105°/0.15 mm., $n = 6$, b.p. 150—170°/0.15 mm., and $n = 14$ and 24 are described.

R. T.

Polymerisation of $\text{C}_n\text{H}_{2n-4}$ hydrocarbons with vicinal double and triple linkings. A. E. FAVORSKI and A. I. ZACHAROVA (J. Gen. Chem. Russ., 1937, 7, 973—976).— $\text{CH}_2\text{C}\cdot\text{CMe}\cdot\text{CHMe}$ in MeOH at 120° (12 hr.) gives 1:2-dimethyl-4- α -methyl- Δ^{α} -propenylbenzene, b.p. 85—87°/10 mm., which yields 1:2:4- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})$, 1:2:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}_2\text{H}$, and AcOH when oxidised (KMnO_4 in aq. KOH).

R. T.

Configurative relationship of alkyl halides with α -halogeno-acids. P. A. LEVENE and A. ROTHEN [with M. KUNA] (J. Biol. Chem., 1937, 119, 189—192).—(—)- γ -Chloro- Δ^{α} -heptene is reduced in MeOH-HCl (Adams; H_2 at 3 atm.) to (+)- γ -chloroheptane, b.p. 87—90°/113 mm., $\alpha_D^{25} +1.46^\circ$. This change of sign had already been observed when passing from (+)- γ -chloro- Δ^{α} -heptene to (—)- α -chloro-

n-hexoic acid (A., 1929, 1272); the active acids of type $\text{CHRCI}\cdot\text{CO}_2\text{H}$ and the structurally related halides CHREtCl thus rotate in the same direction. This confirms previous formulations (Levene and Haller, A., 1929, *passim*).

E. W. W.

Aliphatic chloro-derivatives. VI. Reactivity of polychlorides of the allyl type. D. V. TISCHTSCHENKO. **VII. Chlorination of *sec*-butyl chloride.** **VIII. Chlorination of α -chlorobutane.** D. V. TISCHTSCHENKO and A. TSCHURBAKOV. **IX. Inductive effect and order of substitution of hydrogen by chlorine atoms in saturated hydrocarbons and their chloro-derivatives.** D. V. TISCHTSCHENKO (J. Gen. Chem. Russ., 1937, 7, 658—662, 663—666, 893—896, 897—900).—VI. The products of hydrolysis with an aq. suspension of CaCO_3 of $\text{CMeCl}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ (80°; 7 hr.) are chiefly $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMeCl}$, with $\text{CH}_2\cdot\text{CH}\cdot\text{COMe}$, and of *cis*- and *trans*- $\text{CHMe}\cdot\text{CCl}\cdot\text{CH}_2\text{Cl}$ (90°; 36 hr.) are β -chloro- Δ^2 -buten- α -ol, b.p. 52—53°/19 mm. (α -naphthylurethane, m.p. 95—96°), and γ -chloro- Δ^2 -buten- β -ol, b.p. 67—68°/19 mm. (α -naphthylurethane, m.p. 92—92.5°), whilst $\text{CH}_2\cdot\text{CCl}\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$ is not hydrolysed under these conditions. It is concluded that the presence of α -Cl reduces the mobility of other Cl atoms, and that α' -substitution abolishes reactivity completely.

VII. CHMeEtCl and Cl_2 yield $\alpha\beta$ - (I), $\alpha\gamma$ - (II), $\beta\beta$ - (III), and $\beta\gamma$ -dichlorobutane (IV); Meyer's rule does not therefore apply to this case. (II), but not (I), is readily hydrolysed to butanediol by aq. K_2CO_3 . (III) and (IV) yield $\text{CMeCl}\cdot\text{CHMe}$ when similarly hydrolysed.

VIII. The mixture of dichlorides obtained from Bu^nCl and Cl_2 contains $\alpha\alpha$ - 3, $\alpha\beta$ - 17, $\alpha\gamma$ - 50, and $\alpha\delta$ -dichlorobutane 25%. Meyer's rule is not followed in this case.

IX. The readiness with which H atoms in primary, *sec*-, and *tert*-hydrocarbons are replaced by Cl varies according to the structure of the hydrocarbon, and the no. and position of Cl already present. The results are explained on the basis of the negative and positive induction effects of Cl and alkyl radicals respectively.

R. T.

Photochemical chlorination of *cis*-dichloroethylene to tetrachloroethane and of trichloroethylene to pentachloroethane.—See A., I, 370.

Preparation of polymethylene dihalides with long chains. K. ZIEGLER and H. WEBER (Ber., 1937, 70, [B], 1275—1279).—The difficulty of converting long-chained ethers $\text{OPh}\cdot[\text{CH}_2]_n\cdot\text{OPh}$ into $\text{Hal}\cdot[\text{CH}_2]_n\cdot\text{Hal}$ can be overcome by introducing suitable substituents into the C_6H_5 nucleus. One-sided reaction between $\text{Hal}\cdot[\text{CH}_2]_n\cdot\text{Hal}$ and an equiv. amount of NaOAr is achieved by the use of a solvent in which the former dissolves much more freely than does $\text{OAr}\cdot[\text{CH}_2]_n\cdot\text{Hal}$, the alkali being introduced gradually into the mixture. Gradual addition of $\text{KOH}\cdot\text{MeOH}$ to a mixture of *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ and a large excess of $\text{Br}\cdot[\text{CH}_2]_{10}\cdot\text{Br}$ at 100° gives *p*-anisyl κ -bromodecyl ether, b.p. 190°/0.05 mm., 61—62°, converted by NaI in boiling COMe_2 or MeOH into *p*-anisyl κ -iododecyl ether (I), m.p. 75°, more conveniently obtained by gradual addition of powdered

KOH to $I \cdot [CH_2]_{10} \cdot I$ and $p\text{-OH} \cdot C_6H_4 \cdot OMe$ in Bu^oOH at 35° (yield 90%). (I) is transformed by Na in Et_2O into $\alpha\omega$ -di- p -anisylloxyeicosane, m.p. 121° , transformed by boiling 56% HI into $\alpha\omega$ -di-iodoeicosane, m.p. 71° . H. W.

Nitration of n -paraffins. II. T. URBAŃSKI and M. SŁOŃ (Rocz. Chem., 1937, 17, 161—164).—Mixtures of α -nitro- and $\alpha\omega$ -dinitro-paraffins are obtained on 30—80% yield from NO_2 and $n\text{-C}_5H_{12}$, -C_6H_{14} , -C_7H_{16} , -C_8H_{18} , or -C_9H_{20} at 200° . R. T.

Mechanism and applicability of the Guerbet reaction. C. WEIZMANN, E. BERGMANN, and L. HASKELBERG (Chem. and Ind., 1937, 587—591).—The following mechanism is suggested for Guerbet's condensation of alcohols at high temp. under the influence of Na: $2Pr^oOH \rightarrow 2Pr^oCHO + 2H_2 \rightarrow CHPr^o \cdot CEt \cdot CHO \rightarrow CH_2Pr^o \cdot CHEt \cdot CH_2 \cdot OH$. In the first stage of the change H_2 is set free as such, but the last stage does not require mol. H_2 since large amounts of Bu^oOH are converted into Pr^oCO_2H . NaOEt mainly enhances the condensation of the aldehyde mols. and possibly accelerates the dehydrogenation of the alcohol, which is a purely thermolytic process. Na can therefore be replaced by other mild alkalis. The part played by catalytic influences is established by the increased yield of end products if Cu-bronze is added to the reaction mixture, Bu^oOH , $NaOBu^o$, and Cu-bronze at 210° give unchanged material, Pr^oCO_2H and substances of higher b.p., $Pr^oCO_2Bu^o$, β -ethylhexyl butyrate, b.p. $118\text{—}120^\circ/25$ mm., and β -ethylhexanol (I), b.p. $181^\circ/760$ mm., $90^\circ/26$ mm. (corresponding phenylcarbamate, b.p. $162^\circ/4$ mm., m.p. $33\text{—}34^\circ$). (I) is converted by $SOCl_2$ and $NPhMe_2$ into β -ethylhexyl chloride, b.p. $73^\circ/18$ mm. (corresponding bromide, b.p. $80^\circ/18$ mm.). β -Ethylhexyl iodide, b.p. $90^\circ/18$ mm., and NMe_3 in $PhNO_2$ at room temp. afford trimethyl- β -ethylhexylammonium iodide, m.p. 208° . Benzyltrimethyl- β -ethylhexylammonium iodide, has m.p. 127° . β -Ethylhexylaniline, b.p. $166^\circ/2$ mm. (Ac derivative, b.p. $185^\circ/20$ mm.), and β -ethylhexyl-2-naphthylamine, b.p. $224^\circ/18$ mm., are described. $Et_2\beta$ -ethylhexylmalonate, b.p. $189^\circ/20$ mm., is very smoothly converted by $CH_2 \cdot CH \cdot CH_2 \cdot Br$ and NaOEt in $EtOH$ into Et_2 allyl- β -ethylhexylmalonate, b.p. $205^\circ/18$ mm. Catalytic dehydrogenation of (I) gives α -ethylhexanal (II), b.p. $160^\circ/760$ mm., $65^\circ/25$ mm. [$NaHSO_3$ derivative; 2:4-dinitrophenylhydrazone, m.p. $120\text{—}121^\circ$; (?) semicarbazone hydrochloride, m.p. $144\text{—}145^\circ$]. Oxidation of (I) by CrO_3 or of (II) by Ag_2O yields α -ethylhexoic acid, b.p. $220\text{—}222^\circ/754$ mm. (p -phenylphenacyl ester, m.p. $49\text{—}50^\circ$; amide; Me ester, b.p. $82^\circ/24$ mm.). Condensation of $CH_2Ph \cdot OH$ with Pr^oOH in presence of Na and Cu-bronze at 260° affords β -benzylpropyl alcohol and $BzOH$. α -Benzylpropionic acid, b.p. $160^\circ/12$ mm. (p -phenylphenacyl ester, m.p. 73°), and α -benzylpropaldehyde (2:4-dinitrophenylhydrazone, m.p. 119°) are described. β -Benzylbutanol, obtained from $CH_2Ph \cdot OH$ and Bu^oOH , is dehydrogenated to α -benzylbutaldehyde, b.p. $109^\circ/20$ mm. ($NaHSO_3$ derivative; 2:4-dinitrophenylhydrazone, m.p. 115°). α -Benzylbutyric acid, b.p. $174^\circ/13$ mm., gives a p -phenylphenacyl ester, m.p. $92\text{—}5^\circ$. Condensation of

$p\text{-OMe} \cdot C_6H_4 \cdot CH_2 \cdot OH$ with Bu^oOH affords unchanged materials and β - p -methoxybenzylbutanol, b.p. $138\text{—}140^\circ/1\text{—}5$ mm. $CHPh \cdot CH \cdot CH_2 \cdot OH$ and Bu^oOH give β -cinnamylbutanol, b.p. $110^\circ/0\text{—}8$ mm., and di- γ -phenylpropyl ether, b.p. $147\text{—}150^\circ/1\text{—}8$ mm.; cinnamyl 3:5-dinitrobenzoate has m.p. 125° . cycloHexanol and Bu^oOH yield o -butylcyclohexanol, b.p. $116^\circ/21$ mm. (3:5-dinitrobenzoate, m.p. 73° ; acetate, b.p. $129\text{—}130^\circ/26$ mm.; butyrate, b.p. $180^\circ/27$ mm.), and a substance (annexed formula), b.p. $155\text{—}160^\circ/21$ mm., m.p. $110\text{—}5^\circ$. o -Butylcyclohexanone, b.p. $86^\circ/22$ mm., gives a 2:4-dinitrophenylhydrazone, m.p. $113\text{—}114^\circ$, and a semicarbazone, m.p. $143\text{—}144^\circ$. A by-product, $C_{16}H_{28}O_2$, b.p. $115^\circ/1\text{—}5$ mm., is obtained in the condensation of Bu^oOH with cyclohexanone. o -Propylcyclohexanol, b.p. $195^\circ/750$ mm., $90^\circ/18$ mm., possibly a mixture of isomerides, gives a cryst. 3:5-dinitrobenzoate, m.p. 75° (α -naphthylamine derivative, m.p. 89°); cyclohexyl H 3-nitrophthalate has m.p. 134° . $CH_2Ph \cdot OH$ and cyclohexanol afford o -benzylcyclohexanol, b.p. $165^\circ/18$ mm., m.p. 75° (3:5-dinitrobenzoate, m.p. $134\text{—}5^\circ$; phenylurethane, m.p. 109° ; acetate, b.p. $177^\circ/18$ mm.), and 2:6-dibenzylcyclohexanol (III), b.p. $194^\circ/18$ mm., m.p. 124° (acetate, m.p. 101°). Hydrogenation ($Pd\text{-BaSO}_4$) of 2:6-dibenzylidenecyclohexanone gives 2:6-dibenzylcyclohexanone, m.p. 114° (and its peroxide, m.p. $130\text{—}131^\circ$), reduced by Na in moist Et_2O to (III), stout prisms, m.p. $121\text{—}122^\circ$, or needles, m.p. 101° . Cetyl alcohol and cyclohexanol give unchanged material, palmitic acid, and a non-homogeneous material, m.p. 85° . $CH_2Ph \cdot CH_2 \cdot OH$ and cyclohexanol give mainly polystyrene with Na but in presence of $CH_2Ph \cdot CO_2Na$ afford o - β -phenylethylcyclohexanol, b.p. $125^\circ/0\text{—}4$ mm. (phenylurethane, m.p. $143\text{—}144^\circ$). H. W.

Action of carbon dioxide in the vapour-phase oxidation of alcohol at metallic catalysts. A. M. RUBINSCHTEIN and A. J. KRONROD (J. Appl. Chem. Russ., 1937, 10, 888—899).—The principal reaction taking place between $iso\text{-C}_5H_{11} \cdot OH$ (I), H_2O , and CO_2 in presence of Ag-asbestos at $375\text{—}425^\circ$ is that of oxidation of Bu^oCHO (II), with simultaneous reduction of CO_2 to HCO_2H , which decomposes to yield CO_2 and H_2 . Dehydration of (I) to iso amylene, and oxidation of (II) to Bu^oCO_2H , take place to a limited extent. R. T.

Micro- and submicro-determination and identification of ethyl alcohol. M. NICLOUX (Ann. Ferment., 1936, 1, 449—467; Chem. Zentr., 1936, i, 3375).—The $EtOH$ (0.1—4.6 mg.) is oxidised in a closed tube at 100° with a slight excess of standard $K_2Cr_2O_7\text{-H}_2SO_4$; the excess of reagent is reduced with excess of $FeSO_4$ and this latter titrated with $KMnO_4$. H. N. R.

Electrochemical oxidation of n -butyl alcohol.—See A., I, 419.

Catalytic dehydrogenation of alcohols to yield esters. VI. Mechanism of esterification of iso -amyl alcohol. N. M. ABRAMOV and B. N. DOLGOV (J. Gen. Chem. Russ., 1937, 7, 1009—1014).—The yields of iso amyl $isovalerate$ (I) fall, and of iso valeric acid and aldehyde (II) rise, with increasing

[CO₂] or [N₂] of the reaction mixture, when the latter is passed over a CuO-U₃O₈ catalyst at 280°; the opposite effects are obtained by increasing the [H₂] of the mixture. (I) is obtained in good yield from (II) and H₂ under similar conditions. R. T.

Criegee and Grignard reactions. A. GILLET (Bull. Soc. chim. Belg., 1937, 46, 171—172).—The Criegee reaction is considered to be the inverse of the addition of the Grignard reagent to a ketone.

J. D. R.

Preparation of acetylenic glycols. II. L. KAZARJAN (J. Gen. Chem. Russ., 1937, 7, 956—958).—Glycols, (OH·CRR'·C≡)₂, are obtained from the appropriate ketones with CaC₂ and KOH in Et₂O, at room temp.: R = R' = Me, from COMe₂; R = Me, R' = Ph, from COPhMe; R = R' = Ph, from COPh₂; RR' = cyclohexyl, from cyclohexanone.

R. T.

β-Triphenylmethyl derivatives of glycerol. P. E. VERKADE, J. VAN DER LEE, and (FRL.) W. MEERBURG (Rec. trav. chim., 1937, 56, 613—622).—The ready formation of compounds of this type affords further proof that CPh₃Cl is not sp. for primary OH. α-Monostearin is converted by CPh₃Cl in quinoline at 100° into βγ-diphenylmethylglyceryl α-stearate, m.p. 83.5—84°, also obtained analogously from γ-triphenylmethylglyceryl α-stearate. αγ-Ditriphenylmethylglycerol and stearyl chloride in CHCl₃-quinoline yield αγ-ditriphenylmethylglyceryl β-stearate, m.p. 83—84°, the formation of modifications of lower m.p. being indicated. Glycerol and CPh₃Cl in C₅H₅N at 100° during 3 hr. give αγ-ditriphenylmethylglycerol, m.p. 177—178° (occasionally m.p. 181—182°), transformed by CPh₃Cl in quinoline at 100° during 7 hr. into αβγ-tri(triphenylmethyl)glycerol (+0.5CHCl₃), m.p. 196—197° (also +1CCl₄ and +2C₆H₆).

H. W.

Titration of nitric esters.—See A., I, 425.

Preparation of crystalline β-4-glucosidosorbitol and its monomethyl derivative. P. A. LEVENE and M. KUNA (Science, 1937, 85, 550; cf. this vol., 83).—Reduction (Raney Ni) of cellobiose in H₂O at 75°/100 atm. yields cryst. platelets of β-4-glucosidosorbitol, m.p. 133°, [α]_D²⁵ -8.7° in H₂O. One methylation with Me₂SO₄ by West and Holden's method gave the fully methylated product, b.p. 170°/0.2 mm., [α]_D²⁵ -4.93° in abs. EtOH.

L. S. T.

Thermal decomposition of dimethyl ether.—See A., I, 366.

Explosions attributed to interaction between ethyl peroxide and sulphur. H. F. TAYLOR (Mem. Manchester Phil. Soc., 1937, 81, 15—18).—Conditions favourable for the explosion of Et₂O₂ are infrequent, but presence of S or other readily oxidisable material may cause explosion.

J. W. S.

Molecular compounds of dioxan. V. Dioxanates of the halides of bivalent metals. H. RHEINBOLDT, A. LUYKEN, and H. SCHMITTMANN (J. pr. Chem., 1937, [ii], 149, 30—54).—The following dioxanates (R = C₄H₈O₂) are prepared by crystallisation of the halide from dioxan (I), by pptn. from EtOH by (I), or by displacement of Et₂O from the etherates. Power of addition and stability of the

products increase generally from chloride to iodide and the dioxanates are more stable than the corresponding etherates. CaCl₂.R; CaBr₂.R₂; CaI₂.R₂; SrBr₂.R₂; SrI₂.R₂; BaI₂.R₂, readily decomposed by exposure to light; MgCl₂.R₂, very hygroscopic; MgBr₂.R₂; MgI₂.R₂, decomp. about 150°; ZnCl₂.R₂; ZnBr₂.R₂; ZnI₂.R₂, decomp. about 75—80° in a sealed capillary; CdCl₂.R; CdBr₂.R, decomp. about 200°; CdI₂.R, decomp. about 175—180°; HgCl₂.R, decomp. about 160—165°; HgBr₂.R; HgI₂.R; Hg(CN)₂.R₂, very unstable; Hg(CNS)₂.R; CuCl₂.R; CuBr₂.R; SnCl₂.R; SnBr₂.R; MnCl₂.R; MnBr₂.R₂; MnI₂.R₂; FeCl₂.R₂; FeBr₂.R₂; FeI₂.R₂; CoCl₂.R; CoBr₂.R₂; CoI₂.R₄; CoI₂.R₂; NiCl₂.R₂; NiBr₂.R₂; NiI₂.R₂. Dioxanates could not be obtained from SrCl₂, BaCl₂, and BaBr₂.

H. W.

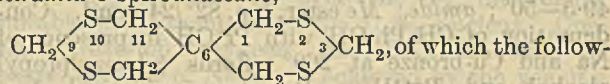
Hydrolysis of monoacid triglycerides under the influence of pancreatic extract.—See A., III, 268.

Preparation of hexose monophosphate from yeast extract.—See A., III, 271.

Monothioformals. F. W. WENZEL, jun., and E. E. REID (J. Amer. Chem. Soc., 1937, 59, 1090—1091).—RSH and CH₂Cl·OR in NaOH-EtOH at room temp. give Et₂, b.p. 135.8°, Pr^a, b.p. 179.2°, and Bu^a monothioformal, b.p. 220°, SR·CH₂·OR. *d*₄²⁰, *d*₄²⁵, and *n*_D²⁵ are recorded. The compounds are stable at the b.p. and react only slowly with Grignard reagents; the Et₂ compound with MgEtBr at 100° gives EtSH and EtOPr, showing that SR is replaced more readily than OR. HCl rapidly decomposes the compounds to the formal and dithioformal; unchanged CH₂Cl·OR must, therefore, be removed from the reaction products before storage. Oxidation proceeds readily, but does not yield a sulphone.

R. S. C.

Tetrathiolmethylmethane (tetrathiopentaerythritol), a reagent for aldehydes and ketones. H. J. BACKER and N. EVENHUIS (Rec. trav. chim., 1937, 56, 681—690).—Reduction of 2:3:7:8-tetrathia-6-spirocyclononane by Na in liquid NH₃ affords tetrathiolmethylmethane (I), m.p. 73—73.5° (Tl, Ag, Hg, Cu, and Pb salts), in 80% yield. It is oxidised by I in EtOH to the dimeric thio-ether, [·S·CH₂·C(CH₂·S)₂·CH₂·S·]₂, m.p. 147.5—148.5°, and by 30% H₂O₂ in AcOH to the tetrasulphonic acid C(CH₂·SO₃H)₄, isolated as the Ba salt. (I) reacts with aldehydes and ketones and HCl, alone or in presence of EtOH, CHCl₃, or mixtures thereof, giving characteristic derivatives of 2:4:8:10-tetrathia-6-spiroundecane,



ing are described: 3:9-dimethyl-, m.p. 110°; 3:9-diacyl-3:9-dimethyl-, m.p. 164—165.5°; 3:9-difuryl-, m.p. 132.5—133°; 3:3:9:9-tetramethyl- (II), m.p. 192—193°; 3:9-dimethyl-3:9-diethyl- (III), m.p. 143—143.5°; 3:3:9:9-tetraethyl-, m.p. 118—118.5°; 3:3-dimethyl-9:9-ditert.-butyl-, m.p. 165—167°; 3:9-diethyl-3:9-ditert.-butyl-, m.p. 177—178°; 3:9-di(tetramethylene)- (IV),

reaction $\text{CH}_3\cdot\text{CH}\cdot\text{CHR} + \text{HBr}$, the reactivity of the unsaturated C atoms is independent of the length of the alkyl chain. J. D. R.

Long-chain carbon compounds. *n*-Tetratriacontanoic and *n*-hexatetracontanoic acids and their derivatives. F. FRANCIS, A. M. KING, and J. A. V. WILLIS (J.C.S., 1937, 999—1004).—Condensation of behenoyl chloride [from behenic acid and $(\text{COCl})_2$ in C_6H_6] with Et sodio- α -acetylbrassylate (I) in Et_2O or C_6H_6 affords μ -ketotetratriacontanoic acid (II), m.p. 107.7° (Et ester, m.p. 80.9°), and λ -acetyl-lauric acid, m.p. 73.5° . (II) when reduced (Clemmensen) affords *n*-tetratriacontanoic acid (III), m.p. 98.2° [Et ester, m.p. 75.4° ; anilide, m.p. 114° ; chloride (IV), m.p. 73.1°], converted (Hell and Sadomsky) into α -bromotetratriacontanoic acid, dimorphic (β -form, m.p. 89.1° ; α -form, m.p. 77.37°), hydrolysed ($\text{KOAc}-\text{AcOH}$) to α -hydroxytetratriacontanoic acid, m.p. $109-110^\circ$. Electrolysis of the K salt of (III) affords *n*-hexaheptacontane, m.p. 103.6° . *n*-Heptaheptacontane-34-one [from (III), by heating with Fe] is reduced (Clemmensen) to *n*-heptaheptacontane, m.p. 104.1° . From (III) by reduction (Bouveault) of the Et ester followed by conversion into the iodide, condensation with $\text{CHNa}(\text{CO}_2\text{Et})_2$, and subsequent hydrolysis is prepared *n*-hexatriacontanoic acid, m.p. 99.9° , [Et ester, m.p. 78.6° , reduced (Bouveault) to *n*-hexatriacontan- α -ol (V), m.p. 92.9°]. Similar stepwise synthesis from (V) affords *n*-octatriacontanoic acid, m.p. 101.6° (Et ester, m.p. 80.55° , reduced to *n*-octatriacontan- α -ol, m.p. 93.6°). (I) and (IV) in dry Et_2O in an atm. of N_2 afford impure ethyl- α -acetyl- α -tetratriacontanoyl brassylate, m.p. $68-90^\circ$, hydrolysed ($\text{EtOH}-\text{KOH}$) to μ -ketoheptacontanoic acid, m.p. 115° (Et ester, m.p. 93.76°), reduced (Clemmensen) to hexatetracontanoic acid, m.p. 107.1° (Et ester, m.p. 90.5°). The crystal spacings of many of these acids and their derivatives are given, and the heat of crystallisation of Et tetratriacontanoate is recorded. J. D. R.

Liquid acids of sapucainha oil. H. PAGET (J.C.S., 1937, 955—960).—The seeds of *Carpotroche brasiliensis*, Endl, yield to CCl_4 sapucainha oil, hydrolysed ($\text{KOH}-\text{EtOH}$) to chaulmoogric (I), hydnocarpic, and palmitic acids, and mixed liquid acids, the Cu salts of which are separated into sol. (A) and insol. (B) in COMe_2 . Distillation of the Me esters of acids (A) yields (fraction of b.p. $185-210^\circ/0.5$ mm.) after hydrolysis ketochoaulmoogric acid,

$\text{CO}-\text{CH} > \text{C} \cdot [\text{CH}_2]_n \cdot \text{CO}_2\text{H}$ (II; $n = 12$), m.p. 116° [semicarbazone, m.p. 157° (decomp.)], and keto-hydnocarpic acid (II; $n = 10$), m.p. 108° [semicarbazone, m.p. 156° (decomp.)]. Ketochoaulmoogric acid with $\text{PtO}-\text{H}_2$ in EtOH affords dihydrochoaulmoogric acid (III) (p-bromoanilide, m.p. 102°) and a dihydroketoacid, $\text{C}_{18}\text{H}_{32}\text{O}_3$ (semicarbazone, m.p. 164°), which is oxidised (KMnO_4) to γ -keto-*n*-pentadecanedicarboxylic acid (IV). The non-volatile Me esters of acids (A) on hydrolysis yield liquid acids (C), hydrogenated (H_2 -Pd- BaSO_4) to (III) and stearic acid. Oxidation (KMnO_4 - KOH) of the acids affords dihydroxystearic acid and tetrahydroxydihydrochoaulmoogric acid, m.p. $111-113^\circ$, $[\alpha]_D^{25} -17.9^\circ$ in EtOH (Me ester, by CH_2N_2 ,

m.p. 88° ; tetramethoxyacetyl derivative of Me ester; tetraphenylurethane, m.p. 145°), further oxidised (H_2CrO_4) to adipic acid (V), a ketone (probably δ -keto-*n*-decane- ω -dicarboxylic acid; semicarbazone, m.p. 187°), and *n*-nonane- α - γ -tricarboxylic acid (Me₃ ester, b.p. $200-217^\circ/15$ mm.; trianilide, m.p. 189°), which latter is further oxidised (H_2CrO_4) to $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, (V), and suberic acid. The liquid acids (C) therefore must contain dehydrochoaulmoogric acid, $\text{CH}_3\cdot\text{CH} > \text{CH} \cdot [\text{CH}_2]_6 \cdot \text{CH} \cdot \text{CH} \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$. Et chaulmoograte or sapucainha oil on long exposure to sunlight and air is oxidised to (II); this explains the occurrence of (IV) in the oxidation products of (I) observed by Barrowcliff and Power (J.C.S., 1907, 91, 557), (II) being an intermediate stage in the oxidation. J. D. R.

Isomerisation of linoleic acid. II. G. V. PIGULEVSKI and I. V. ROKITANSKI (J. Gen. Chem. Russ., 1937, 7, 882—884).—Oxidation of poppy-seed oil with BzO_2H leads to production of the solid and liquid isomerides of the dioxide of linoleic acid (I), and of the oxide of oleic acid. The content of α -isomeride in natural is the same as in synthetic (I). R. T.

Hydnocarpic and chaulmoogric acids and ethyl esters. H. I. COLE and H. CARDOSO (J. Amer. Chem. Soc., 1937, 59, 963—965).—Details are given for the prep. of pure hydnocarpic (I), m.p. 60.5° , $[\alpha]_D^{25} +69.3^\circ$ (Et ester, b.p. $184^\circ/10$ mm., $[\alpha]_D^{25} +61.94^\circ$), and chaulmoogric acid (II), m.p. 68.5° , $[\alpha]_D^{25} +60.3^\circ$ (Et ester, b.p. $206^\circ/10$ mm., $[\alpha]_D^{25} +55.42^\circ$), best from *Hydnocarpus Wightiana* oil [which contains no palmitic acid (III)], the essential step being careful fractionation of the Et esters. The best criteria of purity are $[\alpha]$ and crystal form. Mixed m.p. curves for (I)-(II) and (I)-(III), and d and n for the Et esters at 20° , 25° , and 30° are given. R. S. C.

Odour and constitution. II. Lactones. J. VON BRAUN [with E. ANTON and W. MAY] (Ber., 1937, 70, [B], 1251—1253; cf. A., 1930, 68).—In lactones $\text{CHALK}-\text{CO} > \text{O}$ the intensity of odour attains its max. when 11 C are present if in a straight chain. Branching of the chain causes increase in the intensity. The lactones described below are obtained by the introduction of C_3H_5 into monoalkylmalonic esters, followed by hydrolysis, decarboxylation, and heating with 70% H_2SO_4 . The following are new: *Et*₂ *n*-decylmalonate, b.p. $193-195^\circ/13$ mm.; *Et*₂ allyl-*n*-decylmalonate, b.p. $210-212^\circ/13$ mm.; α -allyldodecoic acid, b.p. $170^\circ/0.3$ mm.; α -*n*-decyl- γ -valerolactone, b.p. $203-205^\circ/16$ mm., m.p. 46° ; *Et*₂ $\gamma\gamma$ -dimethyloctylmalonate, b.p. $183-187^\circ/13$ mm.; *Et*₂ allyl- $\gamma\gamma$ -dimethyloctylmalonate, b.p. $200-203^\circ/13$ mm.; $\delta\delta$ -dimethyl- α -allyldodecoic acid, b.p. $165^\circ/0.1$ mm.; α - $\gamma\gamma$ -dimethyloctyl- γ -valerolactone, b.p. $193^\circ/13$ mm.; *Et*₂ *n*-octylmalonate, b.p. $175-177^\circ/17$ mm.; *Et*₂ allyl-*n*-octylmalonate, b.p. $192^\circ/16$ mm.; α -allyldodecoic acid, b.p. $155^\circ/0.2$ mm.; α -*n*-octyl- γ -valerolactone, b.p. $196^\circ/16$ mm., m.p. 40° ; *Et*₂ *n*-heptylmalonate, b.p. $163^\circ/17$ mm.; *Et*₂ allyl-*n*-heptylmalonate, b.p. $175-180^\circ/17$ mm.; α -allyl-nonoic acid, b.p. $145^\circ/0.5$ mm., α -*n*-heptyl- γ -valero-

lactone, b.p. 170—172°/17 mm.; Et_2 *n*-hexylmalonate, b.p. 152°/17 mm.; Et_2 allyl-*n*-hexylmalonate, b.p. 167°/17 mm.; allyl-*n*-hexylmalonic acid, m.p. 91°; α -allyloctoic acid, b.p. 130°/0.1 mm.; α -*n*-hexyl- γ -valerolactone, b.p. 153°/14 mm.; Et_2 cyclohexylallylmalonate, b.p. 168°/14 mm.; cyclohexylallylmalonic acid, m.p. 127°; α -cyclohexyl- Δ^8 -pentenoic acid, b.p. 152—155°/14 mm.; α -cyclohexyl- γ -valerolactone, b.p. 150—152°/14 mm.; Et_2 allylamylmalonate, b.p. 140—143°/10 mm.; allylamylmalonic acid, m.p. 96—98°; α -allylheptoic acid, b.p. 132—135°/11 mm.; α -*n*-amyl- γ -valerolactone, b.p. 128°/10 mm. H. W.

Course of diene syntheses. K. ALDER and G. STEIN (Angew. Chem., 1937, 50, 510—519).—A summary of recent work on diene polymerisation.

J. W. S.

Biological oxidation of highly unsaturated fatty acids. Preparation of polyenedicarboxylic acids. R. KUHN, F. KÖHLER, and L. KÖHLER (Z. physiol. Chem., 1937, 247, 197—219).—Feeding of sorbic acid to rabbits is followed by excretion of 0.1—0.2% (calc. on amount fed) of *trans-trans*-muconic acid [isolated as Me_2 ester (A., 1936, 1093)]; feeding of *Me* and *Et* sorbate yields 0 and 0.5%, respectively, whilst that of the acid amide affords 32% of *muconamic acid*, m.p. 281—282° (corr., decomp.). Similarly, *sorbomethylamide*, m.p. 141° (corr.) (from the acid chloride and NH_2Me), gives 44% of *muconomethylamic acid*, m.p. 217° (corr., decomp.), *sorbanilide* yields 36% of *muconanilic acid*, m.p. 261—263° (corr., decomp.), and β -methylsorbamic acid, m.p. 136—141° [from the acid (A., 1932, 600)], gives 62% of β -methylmuconamic acid, m.p. 259—261° (corr.). Thus with aliphatic polyenecarboxylic acids, $Me \cdot [CH:CH]_n \cdot CO_2H$, β -oxidation in the organism is diminished by introduction of $CO \cdot NH_2$ and β -*Me* groups. Feeding of crotonanilide yields neither male- nor fumaranilide but 14% of *N*-crotonyl-*p*-aminophenol, m.p. 189—190° (corr.) [also from crotonyl chloride and *p*- $NH_2 \cdot C_6H_4 \cdot OH$; hydrogenated to *N*-butyl-*p*-aminophenol, m.p. 139—140° (corr.), afforded by $BuCl$ and *p*- $NH_2 \cdot C_6H_4 \cdot OH$]. $\beta\beta$ -Dimethylacrylamide, m.p. 110—111° (corr.), yields mesacon- α -amic acid (Anschütz, A., 1907, i, 468) (i.e., only the *Me trans* to the $CO \cdot NH_2$ is oxidised); β -methyl- β -ethylacrylic acid (prepared by condensation of $CH_2Br \cdot CO_2Me$ with $COMeEt$ in presence of Zn to yield *Me* β -hydroxy- β -methylvalerate, b.p. 74—78°/12 mm., which is treated with $ZnCl_2 \cdot Ac_2O$ and the resulting *Me* β -methyl- β -ethylacrylate, b.p. 151—153°, is hydrolysed) and its amide, m.p. 128—128.5° (corr.) (from the acid chloride, b.p. 48°/13 mm.), yield no urinary oxidation acid. The above biological oxidation phenomena also occur with furancarboxylic acids. Thus 5-methylfuran-2-carboxylamide yields 32% of 5-carboxyfuran-2:5-carboxylamide, m.p. 284° (corr.), whilst β -(5-methyl-2-furyl)acrylamide, m.p. 130—131° (corr.) (from the corresponding acid chloride, m.p. 37°, b.p. 124°/9 mm.), gives 83% of 2-(β -acrylamido)furan-5-carboxylic acid, m.p. 280° (corr., decomp.). The acyclic analogue, ζ -methyl- Δ^{ave} -hexatriene- α -carboxylic acid, yields no urinary dicarboxylic acid, but its amide, m.p. 208—209°, affords 42% of α -carboxy- Δ^{ave} -O* (A., II.)

hexatriene- ζ -carboxylamide, decomp. 263° (corr.). Similarly θ -methyl- Δ^{ave} -octatetraene- α -carboxylic acid gives no unchanged or dicarboxylic acid product whilst its amide, m.p. 227° (corr.), affords 20% of α -carboxy- Δ^{ave} -octatetraene- θ -carboxylamide, m.p. approx. 258° (decomp.). The observed pharmacological effects following ingestion of the above compounds are described. F. O. H.

Synthesis of decrocin [Δ^{ave} -tetradecaheptene- $\alpha\zeta$ -dicarboxylic acid]. R. KUHN and C. GRUNDMANN (Ber., 1937, 70, [B], 1318—1333).—It is proposed to base the nomenclature of synthetic compounds resembling carotenoids on the trivial names of the latter whereby the prefix *apo* denotes the presence of one fewer *Me* and “*de*” implies that all side *Me* groups have been removed from the natural material. Crotonaldehyde (I) is condensed by $AcOH$ and piperidine to dodecapentaenal (II), $Me \cdot [CH:CH]_5 \cdot CHO$, m.p. 166°, and octatrienal from which (II) is readily obtained by similar condensation with (I). Condensation of (II) with $CH_2(CO_2H)_2$ takes place in poor yield in presence of C_5H_5N but readily if piperidine is added; similar enhanced yields are observed with all the higher polyene aldehydes but not with the simpler members which thereby suffer increased auto-condensation. Dodecapentaenylidenemalonic acid, $Me \cdot [CH:CH]_5 \cdot CH:C(CO_2H)_2$, is very unsatisfactorily decarboxylated when heated alone or as pyridinium salt, readily in boiling $AcOH \cdot Ac_2O$ to Δ^{ave} -tetradecaheptaenoic acid (III), $Me \cdot [CH:CH]_6 \cdot CO_2H$, m.p. 265—266° (decomp.). Attempted esterification of (III) by treatment with various alcohols and HCl , H_2SO_4 , $KHSO_4$, etc., by CH_2N_2 , $CHMeN_2$, $CHPhN_2$, even with addition of H_2O or $EtOH$, or by treatment of the *Ag* salt with Me_2SO_4 or alkyl halide were unsuccessful but the *Me* ester, m.p. 220°, is obtained by the action of CH_2N_2 in presence of much 96% $EtOH + Et_2O$. Condensation of the ester with $Et_2C_2O_4$ is effected by $KOEt$ or $RbOEt$ in presence of C_5H_5N or quinoline but not of other *tert.* amines, thus giving *Et_2* oxalotetradecaheptaenoate, m.p. 190—191°. The corresponding *Ac* derivative, m.p. 167°, is converted by $Al-Hg$ in $C_6H_6 \cdot Et_2O \cdot H_2O$ into *dedihydrocrocin* *Et_2* ester, m.p. 163—165°, transformed by $NaOEt$ in C_5H_5N into *decrocin* *Et_2* ester, m.p. 217° (corresponding *Me_2* ester, m.p. 236°), which is hydrolysed to *decrocin*, $CO_2H \cdot [CH:CH]_7 \cdot CO_2H$, decomp. >300°. The following new spectroscopic rules are advanced for symmetrical polyenes. CO_2H in conjugation is equiv. to one conjugated ethylenic linking. Conjugated *Ph* corresponds with 1.5 conjugated ethylenic linkings. *Me* attached to the polyene chain is equiv. to 0.25 double linking. A conjugated cyclic double linking is equiv. to 0.5 aliphatic ethylenic linking. H. W.

“Green” ethyl tartrate. T. S. PATTERSON and A. H. LAMBERTON (J.C.S., 1937, 963—964).—When air is aspirated through hot Et_2 tartrate (I), a volatile inactive aldehyde is formed, with Et_2 diketosuccinate (II) (*bis*-2:4-dinitrophenylhydrazone, decomp. 180°) (formed *via* *Et* hydroxyketosuccinate) to which is due the green colour which appears on heating and disappears on cooling (I). Similar aspiration of Bu_2 tartrate yields a green colour, due to Bu_2 diketo-

succinate. The colour change on heating and cooling may be due to hydration. J. D. R.

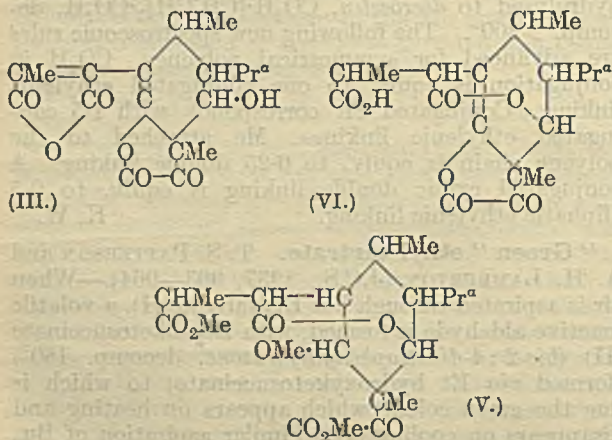
Calcium citrate complexes. C. ARTOM and G. SARZANA (Boll. Soc. ital. Biol. speriment., 1936, 11, 1029—1031).—The dialysis of aq. $\text{CaCl}_2 + \text{Na citrate}$ at p_{H} 6.7—7.6 and 0° with parchment membranes against H_2O or aq. KCl or CaCl_2 indicates the formation of semi-colloidal complexes of Ca citrate.

F. O. H.

Salts of gluconic acid. S. V. NILKANTUM (J. Sci. Tech. India, 1936, 2, 39—51).—Colour, shape, m.p., solubility in H_2O and EtOH , and $[\alpha]_{\text{D}}$ are recorded for the following salts: Mg, K, Na, Mn, Co, Cd, Cr, NH_4 , Al, Cu, Ag, Pb, Ba, Zn, Bi, Fe^{+++} , Fe^{++} , Ca, quinine, berberine, brucine, strychnine, ephedrine, NH_2Ph , and $\text{CO}(\text{NH}_2)_2$.

F. R. G.

Constitution of gluconic acids. VI. K. KRAFT (Annalen, 1937, 530, 20—33; cf. this vol., 109).—Glaucanin (I) and HI-red P at 140 — 150° give by reduction and hydrolysis dihydroglauconinic acid (II), $\text{C}_{11}\text{H}_{12}\text{O}_7$, m.p. 199 — 200° , which titrates tetrabasic when heated; this is stable to O_3 , but its Me ester with O_3 -AcOH gives methyltricarballic acid. This and known data prove the structures $\text{CO} \begin{smallmatrix} \text{CMe} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CMe} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{smallmatrix} \text{CO}$ (I) and $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (II). Hydrogenation (PtO_2) of the Me₂ ester of (I) gives a product, hydrolysed by NaOH to an acid, $\text{CO} \begin{smallmatrix} \text{CMe} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CH}(\text{OMe}) \cdot \text{CHMe} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, m.p. 195° . (I), (II), and gluconic acid (III) give only a little CO with H_2SO_4 . With hot NaOH-Me₂SO₄ (III) affords by hydrolysis of an anhydride ring the Me₂ ester (IV), $\text{C}_{20}\text{H}_{26}\text{O}_8$, m.p. 185° , which by hydrogenation and subsequent hydrolysis gives tetrahydroglauconic acid, $\text{C}_{18}\text{H}_{24}\text{O}_7$, m.p. 178 — 180° , which titrates as a tribasic acid when heated, but with hot Me₂SO₄-NaOH gives the Me₃ ester (V), $\text{C}_{21}\text{H}_{30}\text{O}_8$, m.p. 112° , with some Me₁ ester, m.p. 201° . (IV) gives a Bz derivative, m.p. 177° , which is stable to O_3 , thus proving a difference in the position of the second ethylenic linking in (I) and (III). These and facts already reported support the following formulæ and that for dihydroglauconic acid (VI).



R. S. C.

Preparation and properties of alkyl thioacetates. F. W. WENZEL, jun., and E. E. REID (J. Amer. Chem. Soc., 1937, 59, 1089—1090).—The following n-alkyl thioacetates (alkyl acetylmercaptans) are prepared from the alkyl mercaptans by (a) AcCl , (b) hot Ac_2O - NaOAc (best for the higher members), or (c) Ac_2O in conc. aq. NaOH (best for volatile mercaptans): Me, b.p. 98° , Et, b.p. 116.4° , Pr, b.p. 139.8° , Bu, b.p. 163.4° , amyl, b.p. 185.1° , hexyl, b.p. 205.8° , heptyl, b.p. 227.4° , and octyl, b.p. 247° . n_{D}^{25} , d_4^{25} , and d_4^{20} are recorded.

R. S. C.

Thiolacetic acids and methyl sulphate. B. HOLMBERG (Arkiv Kemi, Min., Geol., 1937, 12, A, No. 11, 27 pp.).— $\text{SR} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (1/40 mol.) in aq. NaOH (a/40 mol.) with Me_2SO_4 (2/40 mol.) give $\text{OH} \cdot \text{SMeR} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (identified through HgCl_2 additive compounds) in amounts varying with the $[\text{NaOH}]$; the % yields in parenthesis are for $a = 3, 2, 1$, and 0 . $\text{R} = \text{Me}$ [compound, $\text{SMe}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot 6\text{HgCl}_2$, m.p. 188 — 189° (decomp.)] (58, 100, 100, 100); Et (48, 87, 100, 90); Pr^a [compound, $\text{SMePr}^a\text{Cl} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot 6\text{HgCl}_2$, m.p. 137 — 138° (decomp.)] (56, 90, 99, 91); Pr^g [compound, $\text{SMePr}^g\text{Cl} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot 6\text{HgCl}_2$, m.p. 173° (decomp.)] (44, 84, 97, 81); Bu^v (30, 62, 100, 100); Ph [compound, $\text{SMePhCl} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot 3\text{HgCl}_2$, m.p. 121 — 123° (decomp.)] (11, 63, 73, 33); CH_2Ph (I) (48, 89, 94, 67); CHPhMe (II), (36, 85, 90, 65); $\text{CH}_2 \cdot \text{CH}_2\text{Ph}$ (60, 94, 100, 95), and $\text{CH}_2 \cdot \text{CH} \cdot \text{CHPh}$ (20, 84, 90, 60). The sulphonium compounds are decomposed in neutral, acid, or alkaline solution by rise of temp., yielding $\text{SMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ and ROH . (I) in addition affords $\text{CH}_2\text{Ph} \cdot \text{SMe}$ and (?) $\text{CH}_2\text{Ph} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ (or $\text{SMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{CH}_2\text{Ph}$) whilst (II) yields $\text{CHPhMe} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ and $\text{SMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{CHPhMe}$ in neutral solution and styrene in alkaline solution.

F. N. W.

Fission of disulphides by alkali. IV. Mode of reaction of tertiary mercaptans and their disulphides. A. SCHÖBERL (Ber., 1937, 70, [B], 1186—1193; cf. A., 1936, 1232).—The determination of SH by 18-phosphotungstic acid is described. $\text{SH} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ does not react with I in acid solution and irregularities are observed with $\text{SH} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$. In alkaline solution the acids are smoothly oxidised to $\alpha\alpha'$ -dimethyl- $\alpha\alpha'$ -dithiopropionic acid, m.p. 198° , which is stable towards alkali and tetraphenyldithiodiacetic acid (I), decomp. (indef.) 185 — 186° , respectively. (I) is transformed by NaOH into $\text{SH} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{OH}$ and $\text{OH} \cdot \text{S} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$ which passes into CSPH_2 , H_2O , and CO_2 .

H. W.

Separation of dl- α -methylthiolpropionic acid into its optical antipodes. A. MELLANDER (Arkiv Kemi, Min., Geol., 1937, 12, B, No. 27, 8 pp.).—Resolution is effected through the quinine salt (+0.33 H_2O), m.p. 153.4 — 154.6° , or brucine salt (+3 H_2O), m.p. 159.4 — 160.4° , of the l-acid, $[\alpha]_{\text{D}}^{25} -81.2^\circ$ in H_2O , and the quinidine salt, m.p. 83.4 — 84.8° , of the d-acid, $[\alpha]_{\text{D}}^{25} +81.1^\circ$ in H_2O .

F. N. W.

Active racemate from $\alpha\alpha'$ -dithio- and $\alpha\alpha'$ -diseleno-dipropionic acid. A. FREDGA (Arkiv Kemi, Min., Geol., 1937, 12, B, No. 22, 8 pp.).—M.p. diagrams of diseleno- (I) and dithio-propionic acid (II) are given as follows: +(I) and -(II), +(I) and +(II), -(I) and +(I), +(II) and -(II), and +(I) -(II),

and $+(II) - (II)$. $+(I) - (II)$ and $+(II) - (II)$ from a continuous series of mixed crystals whilst $+(I)$ and $-(II)$ form a 1 : 1 mol. compound.

F. N. W.

Determination of sensitivity of certain colour reactions for aldehydes and ketones. V. M. PLATKOVSKAJA and S. F. VATKINA (J. Appl. Chem. Russ., 1937, 10, 955—959).—The lowest concns. detectable with $(NH_4)_2MoO_4$ and 50% HCl are: PhCHO 0.0005, citral 0.005, citronellal 0.05, anisaldehyde, cinnamaldehyde, CH_2O , chloral hydrate, and $COMe_2$ 0.5, $o-OH-C_6H_4-CHO$ 1, and $COMeEt$ and $COPhMe$ 5%. The colorations given with phosphomolybdic acid and aq. NH_3 , or $m-C_6H_4(NO_2)_2$ and KOH, are less intense.

R. T.

Spontaneous polymerisation of liquid propaldehyde. E. J. BUCKLER (J.C.S., 1937, 1036).—EtCHO spontaneously polymerises to a substance of no definite b.p. and with mol. wt. corresponding with 2.8 EtCHO units. The second stage of polymerisation yields a volatile portion, $(EtCHO)_x$, and a non-volatile liquid, corresponding with 2.7 methylethylacetaldehyde units. The results suggest aldol condensation. No effective stabiliser of EtCHO is known.

F. R. S.

Transposition of aldoximes under the influence of Raney's nickel. R. PAUL (Bull. Soc. chim., 1937, [v], 4, 1115—1121).—This reaction (cf. this vol., 152; also observed with $Me-[CH_2]_5-CH:N\cdot OH$) can be used for prep. of amides; it is ascribed to presence of Fe and Al with the Ni.

E. W. W.

Raman spectra of deuterium compounds of the type $CD_3\cdot CO\cdot X$.—See A., I, 345.

Use of deuterio-compounds as indicators for the presence of free radicals in organic decomposition reactions. E. W. R. STEACIE and W. A. ALEXANDER (J. Chem. Physics, 1937, 5, 372).—Mixtures of $CO(CD_3)_2$ and Me_2O were heated at 590° for 5 min. and the H_2 was separated and analysed in an attempt to establish the course of decomp. of these substances. The general courses are $CO(CD_3)_2 = CD_4 + CD_2 + CO = CD_4 + CO + 0.5C_2D_4$, and $Me_2O = CH_4 + CH_2O =$ either (i) $CH_4 + CO + H_2$ or (ii) $CH_4 + H + CHO$. Thus if (i) is correct the H_2 should be "light," whereas if (ii) is correct the probability of the H atom extracting another atom from the ether or from the ketone is equal and the resulting H should be approx. 25% "heavy." The mean D content is 3.3% and it is concluded that CH_2O does not decompose by a free radical mechanism. The mechanism suggested by Fletcher and Rollefson (A., 1937, I, 36) for the decomp. of CH_2O through sensitisation by Me radicals from the ether decomp. also involves H atoms and is therefore probably wrong.

W. R. A.

Isomerism of $\alpha\beta$ -ethylenic ketones. I. *iso*-Butylideneacetone. R. HEILMANN (Bull. Soc. chim., 1937, [v], 4, 1064—1071).—Interaction of *iso*-butaldehyde with $COMe_2$ affords sometimes *cis*- and sometimes *trans*- β -methyl- Δ^7 -hexen- ϵ -one (I) (identified as their semicarbazones). Dehydration of β -methylhexan- δ -ol- ϵ -one (II) with $H_2C_2O_4$ leads to analogous conflicting results (cf. A., 1930, 893; J.C.S., 1920, 117, 324; A., 1913, i, 1165). (I) with

$MgEtBr$ and $MgPr^aBr$ affords respectively 50—55 and 70—75% of enol (cf. A., 1930, 67) and after boiling with dil. H_2SO_4 which eliminates the enol form from (I), 25—35 and 60% of enol, respectively. (I) with $N_2H_4\cdot H_2O$ affords 5-methyl-3-isopropylpyrazoline, b.p. $76-78^\circ/11$ mm., [oxidised to (I)], and its azine, which when hydrolysed gives (I) and a little Me *iso*amyl ketone. The crude product obtained by interaction of (I) with $N_2H_4\cdot H_2O$ with H_2SO_4 affords β -methyl- Δ^8 -hexen- ϵ -one, the semicarbazone of which on hydrolysis (conc. $H_2C_2O_4$) gives a ketone, b.p. $152-153^\circ/745$ mm. These reactions with $NH_2\cdot CO\cdot NH\cdot NH_2$ are interpreted in the light of the isomerism of the double linking.

J. L. D.

***iso*Amylideneacetone.** R. HEILMANN (Compt. rend., 1937, 204, 1345—1346).— $COMe_2$ with *iso*valeraldehyde affords Me δ -methyl- Δ^a -pentenyl ketone (I) which with $NH_2\cdot CO\cdot NH\cdot NH_2$ gives a semicarbazido-semicarbazone, m.p. 205° , a monosemicarbazone (II), m.p. $113-114^\circ$, and a gum (III) which probably contains other stereoisomeric forms of (II). Hydrolysis of (II) affords (I), which yields the same products with $NH_2\cdot CO\cdot NH\cdot NH_2$. When (II) is heated it affords 2-carbamyl-5-methyl-3-isobutylpyrazoline (IV). (III) with boiling dil. acid affords (IV) and 5-methyl-3-isobutylpyrazoline, b.p. $91-92^\circ/10$ mm., which when oxidised and then hydrolysed gives Me *isohexyl* ketone.

J. L. D.

Isomerism of $\alpha\beta$ -ethylenic ketones. II. *iso*-Amylideneacetone. R. HEILMANN (Bull. Soc. chim., 1937, [v], 4, 1072—1080; cf. preceding abstract).— $MgBu^aBr$ with $CH(OEt)_3$ affords $\delta\delta$ -diethoxy- β -methylbutane, hydrolysed (dil. H_2SO_4) to *isovaleraldehyde* (semicarbazone, m.p. $131-132^\circ$); this with $COMe_2$ followed by removal of H_2O gives pure β -methyl- Δ^8 -hepten- ζ -one (I), which with $NH_2\cdot CO\cdot NH\cdot NH_2$ affords a semicarbazone (II), m.p. $113-114^\circ$, and another product, gradually converted by recrystallisation into (II) and a gum (III). Hydrolysis of (II) with $H_2C_2O_4$ gives a ketone which with $NH_2\cdot CO\cdot NH\cdot NH_2$ reacts exactly as does (I) and indicates that Me β -isobutylidene-ethyl ketone is not an impurity in (I) which gives rise to (III). When (II) is heated to near its m.p., part of it is changed to a gum, hydrolysed to (I) and an unhydrolysable residue (a pyrazoline?) which is oxidised to a ketone [semicarbazone, m.p. $153-154^\circ$ (IV)]. (III) probably contains 2-carbamyl-5-methyl-3-isobutylpyrazoline, a cyclised form of (I), for it is hydrolysed (HCl) to 5-methyl-3-isobutylpyrazoline, which is oxidised spontaneously to Me *isohexyl* ketone [semicarbazone, m.p. $153-154^\circ$, identical with (IV)].

J. L. D.

(A) Alkylation of ketones by means of sodamide. Propylation of ketones. (B) Synthesis of *tert*-alcohols of the general formulæ $OH\cdot CMe_2\cdot CHR_2$ and $OH\cdot CMe_2\cdot CR_3$, by the action of magnesium methyl bromide on highly branched ketones. I. N. NAZAROV (J. Gen. Chem. Russ., 1937, 7, 688—692, 693—701).—(A) Pinacolin in C_6H_6 is boiled with $NaNH_2$ until evolution of NH_3 ceases, when Pr^aI is added, to yield $\beta\beta$ -dimethylheptan- γ -one, b.p. $168-170^\circ$, which when similarly treated gives $\beta\beta$ -dimethyl- δ -propylheptan- γ -one, b.p. $211-213^\circ$.

$\beta\beta\gamma$ -, b.p. 178—181°, and $\beta\delta\delta$ -tri-, b.p. 178—181°, and $\beta\delta\delta$ -tetra-methylheptan- γ -one, b.p. 193—196°, $\delta\delta\zeta$ -tetramethylnonan- ε -one, b.p. 229—232°, $\beta\delta\delta$ -tetra-, b.p. 170—173°, and $\beta\delta\delta$ -penta-methylhexan- γ -one, b.p. 195—197°, and γ -dimethyl-, b.p. 170—173°, and γ -dimethyl- γ -ethyl-heptan- δ -one, b.p. 204—207°, have been prepared analogously.

(B) The following alcohols have been prepared from the above (and similar ketones) by the Grignard reaction: $\beta\beta\gamma\delta$ -, b.p. 190—193°, and $\beta\gamma\delta\delta$ -tetramethyl-, b.p. 197—199°, $\beta\beta\gamma$ -trimethyl- δ -ethyl-, b.p. 208—211°, $\beta\beta\gamma\delta$ -, b.p. 207—210°, and $\beta\beta\gamma\delta\delta$ -pentamethyl-, b.p. 237—240°, $\beta\beta\gamma$ -trimethyl- $\delta\delta$ -diethyl-, b.p. 252—256°, and $\beta\beta\gamma\delta\delta$ -hexamethyl-hexan- γ -ol, b.p. 235—238°, $\gamma\delta$ -trimethyl- γ -ethyl-, b.p. 235—238°, and $\gamma\gamma\delta$ -penta-methyl-heptan- δ -ol, b.p. 243—246°, $\beta\beta\gamma$ -trimethyl- δ -propyl-, b.p. 234—237.5°, $\beta\beta\gamma\delta$ -, b.p. 212—215°, and $\beta\gamma\delta\delta$ -tetramethyl-, b.p. 215—217°, and $\beta\beta\gamma\delta\delta$ -penta-methyl-heptan- γ -ol, b.p. 233—235°, and $\delta\delta\zeta$ -penta-methylnonan- ε -ol, b.p. 266—269°. R. T.

(A) Action of magnesium *tert*-butyl chloride and magnesium butyl bromide on ethyl isovalerate and butyrate. A. D. PETROV and M. S. MALINOVSKI. (B) Action of magnesium *sec*-propyl chloride, *sec*-butyl bromide, and *sec*-amyl chloride on ethyl octoate. A. D. PETROV and D. N. ANDREEV (J. Gen. Chem. Russ., 1937, 7, 565—569, 570—575).—(A) MgBu^tCl yields COBu^tBu^t and COBu^t , with $\text{Bu}^t\text{CO}_2\text{Et}$ (I) in Et_2O , and COPr^aBu^t and COPr^a , with $\text{Pr}^a\text{CO}_2\text{Et}$ (II). MgBu^aBr (III) gives *di-n-butylisobutylcarbinol*, b.p. 140—145°/10 mm., with (I), and $\text{CPr}^a\text{Bu}^a_2\text{OH}$ with (II). It is concluded that anomalous formation of ketones in place of the expected *tert*-alcohols is associated with presence of Bu^t in the Grignard reagent.

(B) $n\text{-C}_7\text{H}_{15}\text{CO}_2\text{Et}$ (IV) and (III) in Et_2O yield *di-n-butyl-n-heptylcarbinol*, b.p. 131—135°/5 mm., which gave a mixture of ε -*n-butyl- Δ^6* - and Δ^6 -*dodecene*, b.p. 261—267°, when dehydrated by heating with $\text{H}_2\text{C}_2\text{O}_4$ or K xanthate. (IV) yields chiefly $\text{CO}(\text{C}_7\text{H}_{15})_2$ (V), together with *sec*-amyl heptyl ketone, with *sec*- $\text{C}_5\text{H}_{11}\text{MgCl}$, (V) and *sec*-butyl heptyl ketone with MgBu^tBr , and (V) and Pr^t heptyl ketone with MgPr^tCl . R. T.

Hydrogenation of certain oximes by the aid of Raney's nickel. R. PAUL (Bull. Soc. chim., 1937, [v], 4, 1121—1125).—In the hydrogenation of aldoximes at room temp. and normal pressure, Raney's Ni behaves normally, giving primary, *sec*., and (?) *tert*. amines; with $\text{CMe}_2\text{N}\cdot\text{OH}$, $\text{CMeEtN}\cdot\text{OH}$, $\text{CPhMeN}\cdot\text{OH}$, $\text{CPh}_2\text{N}\cdot\text{OH}$, and cyclohexanoneoxime, at 70—85°/50—60 atm., however, only primary amines are formed. E. W. W.

Dichromate method of determination of reducing sugars. S. M. STREPKOV (Ukrain. Chem. J., 1937, 12, 105—113).—10 ml. of solution are heated for 15 min. at 100° with 20 ml. of 0.02N- $\text{K}_3\text{Fe}(\text{CN})_6$ in 4% Na_2CO_3 , the solution is cooled, 15 ml. of 5% H_2SO_4 are added, and the solution is titrated with 0.05N- $\text{K}_2\text{Cr}_2\text{O}_7$ (NHPh_2 indicator). R. T.

Action of organic bases on sugars and their derivatives. H. VOGEL (Ber., 1937, 70, [B], 1193—1202).—When heated with a 10-fold excess of piper-

idine (I) glucose yields solutions with a powerful reducing action towards methylene-blue and dichlorophenol-indophenol which disappears when the solution is acidified. $\text{C}_5\text{H}_5\text{N}$ does not behave analogously. The formation of 1-piperidylglucose is considered inadequate to account for the properties of the compound and the formation of 1:2-dienolglucose-1-piperidide is postulated. Protracted heating of the solution causes decomp. into strongly coloured materials. Similar reducing dienols are derived from fructose, mannose, galactose, lactose, and maltose whereas sucrose (II), raffinose, starch, inulin, cellulose, β -glucosan, α - and β -methylglucoside are indifferent. [The sparing solubility of (II) in boiling (I) can be used for its separation from other sugars, particularly from hexoses.] The free 1:2-dienols are obtained when the sugars are warmed with (I) in H_2O . Monocarboxylic acids and their esters derived from sugars do not give enols with (I). Analogously to the production of ascorbic acid from esters of α -keto-acids, glucosone hydrate tetra-acetate acquires when treated with (I) a greatly enhanced activity which persists for a time in acid solution but ultimately diminishes and almost disappears. Betaine and CNS-compounds have no enolising action whereas salts of guanidine closely resemble (I). Sugar acetates suffer partial loss of Ac and afford enols. Hexose anhydrides with bridge between $\text{C}_{(1)}$ and any other C are not enolised and *al*-glucose penta-acetate does not afford reducing substances in acid or alkaline medium.

H. W.

Crystalline acetal derivatives of *d*-arabinose. (Miss) E. M. MONTGOMERY, R. M. HANN, and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 1124—1129).—With 3:7 $\text{AcOH-Ac}_2\text{O}$ containing 8% of ZnCl_2 β -methyl-*d*-arabinoside triacetate gives by slow acetylating rupture of the ring an approx. 1:1 mixture of two isomeric *d*-arabinose *Me semiacetal penta-acetates* (I) and (II), m.p. 76° and 68—70°, $[\alpha]_D^{20} + 26.9^\circ$ and $+ 34.7^\circ$ in CHCl_3 , respectively; 0.16% of H_2SO_4 in the same solvent gives rapidly the same two penta-acetates with 8% of the cyclic β -*d*-arabinose tetra-acetate, $[\alpha]_D^{20} - 147.2^\circ$; 4% of H_2SO_4 in the same solvent causes complete hydrolysis of OMe, giving 11% of the tetra-acetate and 56% of *aldehydo-d*-arabinose *hexa-acetate*, m.p. 89.5° (corr.), $[\alpha]_D^{20} + 28.1^\circ$ in CHCl_3 . The same mixtures are obtained from pure (I) or (II) by the appropriate reagents. With AlCl_3 in CHCl_3 (I) and (II) yield isomeric 1-chloro-*d*-arabinose *Me semiacetal 2:3:4:5-tetra-acetates*, m.p. 70° and 73° (corr.), $[\alpha]_D^{20} + 28.8^\circ$ and $+ 52.5^\circ$ in CHCl_3 , respectively, both converted by $\text{Ag}_2\text{O-MeOH}$ into *d*-arabinose *Me_2 acetal tetra-acetate*, m.p. 80° (corr.), $[\alpha]_D^{20} + 21.8^\circ$ in CHCl_3 , and thence by $\text{MeOH-Ba}(\text{OMe})_2$ into *d*-arabinose *Me_2 acetal*, m.p. 122°, $[\alpha]_D^{20} - 18.5^\circ$ in H_2O , and finally (HCl) into *d*-arabinose and methyl-*d*-arabinosides. R. S. C.

Crystalline α -methyl-*d*-arabinofuranoside. (Miss) E. M. MONTGOMERY and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 992—993).—When the reaction of *d*-arabinose with MeOH-HCl is stopped at the time of max. positive $[\alpha]$, there is obtained 9% of α -methyl-*d*-arabinofuranoside, m.p. 65—67°, $[\alpha]_D^{20} + 123^\circ$ in H_2O , the structure of which is proved

by its rapid hydrolysis by aq. acid and by HIO_4 -Br degradation (see below). R. S. C.

Two new methyl-*l*-fucoside triacetates. J. MINSAAS (Rec. trav. chim., 1937, 56, 623—626).— α -Methyl-*l*-fucoside is converted by Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at 0° into α -methyl-*l*-fucoside triacetate, m.p. 74° , $[\alpha]_D^{20} -151^\circ$ in CHCl_3 . β -Methyl-*l*-fucoside triacetate has m.p. 99° , $[\alpha]_D^{20} +7.0^\circ$ in CHCl_3 . H. W.

Two forms of anhydrous *l*-rhamnose. Preparation of crystalline *l*-rhamnose β -tetra-acetate. E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 1076—1078).—Rhamnose monohydrate with hot $\text{BaO} \cdot \text{COMe}_2$ or dry EtOH gives a form (I), m.p. $112.5\text{—}113.5^\circ$ (corr.), $[\alpha]_D^{20} +14.6^\circ \rightarrow +8.9^\circ$ in H_2O , which, when seeded in COMe_2 , affords β -rhamnose (II), anhyd., m.p. $123.5\text{—}124.5^\circ$ (corr.), $[\alpha]_D^{20} +38.4^\circ$ in H_2O [tetra-acetate, m.p. $98.5\text{—}99^\circ$, $[\alpha]_D^{20} +13.4^\circ$ in CHCl_3 , prepared in 89% yield by $\text{Ac}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$ at -12° to 0° , or in 43% yield from (I)]. (I) is an $\alpha\beta$ mol. compound, 1:1 if the above $[\alpha]$ for (II) is correct, 3:2 if Minsas' val., $+44^\circ$ (A., 1934, 1337), for (II) is correct. R. S. C.

Configuration of the pyranoses in relation to their properties and nomenclature. H. S. ISBELL (J. Res. Nat. Bur. Stand., 1937, 18, 505—534).—Methods of comparison of the optical rotation, mutarotation, and Br oxidation measurements originally employed with the hexoses (A., 1930, 581) have been extended to the heptoses, and reveal similarities in the properties of sugars classified in the following groups: α -*l*-arabinose, α -*l*-fructose, α -*d*-galactose, α -*d*- α -mannoheptose, and α -*l*- β -galoheptose; β -*l*-arabinose, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, β -*d*-galactose and β -*d*- α -mannoheptose; β -*d*-glucose and β -*l*- β -galoheptose; α -*d*-lyxose, α -*d*-mannose, and α -*l*- α -galoheptose; β -*d*-gulose and β -*d*- α -glucoheptose; β -*d*-idose and β -*d*- β -glucoheptose. The evidence suggests that the pyranose ring is strainless and dissymmetric, and that the sugars in each group have similar ring conformations. The structural characteristics of the α - and β -sugars are discussed in relation to their reactions and nomenclature. α -, $[\alpha]_D^{20} +120^\circ$, and β -*d*- α -mannoheptose are described. F. N. W.

Molecular refraction of α -*d*-galactose. C. N. RÜBER and N. A. SØRENSEN (Kgl. Norske Videns. Selsk. Skr., 1935, No. 22, 24 pp.; Chem. Zentr., 1936, i, 3513).—The difference in mol. refraction for α -methylgalactoside and α -galactose is 7.49, as with other sugars. H. N. R.

Determination of invert sugar (and other reducing sugars) without filtration of cuprous oxide. E. ROBOZ-ROSENBLÜH and G. VAVRINECZ (Magyar chem. Fol., 1935, 41, 192—195; Chem. Zentr., 1936, i, 3374).—An iodometric method is described. H. N. R.

Ketone sugar series. VII. Action of titanium tetrachloride on the methylfructoside acetates. E. PACSU and F. B. CRAMER (J. Amer. Chem. Soc., 1937, 59, 1059—1062; cf. this vol., 230).— β -Methylfructoside tetra-acetate and TiCl_4 in CHCl_3 give a yellow halochromic salt, from which only the original β -tetra-acetate is recovered. The α -tetra-acetate gives β -acetochlorofructose (I) and some unchanged

material, but no β -tetra-acetate. The "ortho-ester" form of methylfructoside tetra-acetate with TiCl_4 gives (I) and with $\text{HBr} \cdot \text{AcOH} \cdot \text{CHCl}_3$ gives β -acetobromofructose. The "ortho-ester" methylmaltoside hepta-acetate with TiCl_4 gives α -acetochloromaltose and with HBr gives α -acetobromomaltose. The acetohalogeno-derivatives of fructose and turanose probably have normal structure, but the structure of turanose is doubtful. R. S. C.

Preparation of penta-acetylketofructose. F. B. CRAMER and E. PACSU (J. Amer. Chem. Soc., 1937, 59, 1148).—Prep. of ketofructose penta-acetate by ZnCl_2 and Ac_2O in 50% yield is described. For high yields conditions must be those facilitating preliminary formation of the β -tetra-acetate.

R. S. C.

Reactions in concentrated sulphuric acid. II. Influence of gases.—See A., I, 417.

New disaccharide, labiose. S. M. STREPKOV (Ber., 1937, 70, [B], 1166—1167).—Extraction of the root nodules of *Eremostachys labiosa* with boiling 96% EtOH affords labiose (I), m.p. $156\text{—}157^\circ$, $[\alpha]_D^{18} +140.82^\circ$ in H_2O (non-mutarotatory). (I) is not fermentable with yeast and reduces Fehling's solution only after hydrolysis with dil. HCl at about 68° . It is oxidised by HNO_3 (d 1.15) at $69\text{—}70^\circ$ to mucic acid. It is derived from 1 mol. of galactose and 1 mol. of a ketose. H. W.

Cleavage of the carbon chain of glucosides by oxidation. Method for determining ring-structures and α - and β -configurations of glucosides. E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 994—1003).—The ring-structure of glucosides is determined by oxidation by HIO_4 to dialdehydes, which with aq. Br in the presence of metallic carbonates give salts of dicarboxylic acids retaining the ether linking originally present in the glucoside. If C is removed during the oxidation, this is disclosed by the amount of HIO_4 consumed. Structures assigned to the resultant acids are confirmed by hydrolysis. The ring-structures thus assigned are in harmony with the results of methylation. α -Methyl-*d*-aldohexopyranosides afford the same *Sr D'*-methoxy-*D*-hydroxymethyldiglycollate (I), $\text{Sr} \langle \text{O} \cdot \text{CO} \text{—} \text{C}^* \text{H} (\text{OMe}) \rangle \text{O}$,

$[\alpha]_D^{20} -53^\circ$ in H_2O (corresponding acid, not isolated, $[\alpha]_D^{20} +25.5^\circ$ in H_2O), examples investigated being α -methyl-*d*-manno- (II), -galacto-, -gluco-, and -gulo-pyranoside. The prefix *D'* (or *L'*) refers to the Fischer nomenclature of $\text{C}_{(1)}$ of the glucoside and the C marked * in (I); *D* (or *L*) refers to the other C to which the ethereal O is attached. The syrupy dialdehyde, $\text{CHO} \cdot \text{CH} (\text{OMe}) \cdot \text{O} \cdot \text{CH} (\text{CHO}) \cdot \text{CH}_2 \cdot \text{OH}$, produced as intermediate product in the above cases has $[\alpha]_D^{20}$ about $+120^\circ$. This limits the ring-structure of the above glucosides to the pyranoside or septanoside type; the former is indicated by formation of α -methyl-*d*-mannuronic acid [*brucine*, m.p. 232° (decomp.), $[\alpha]_D^{20} -2.5^\circ$ in H_2O , and K salt, $+0.5\text{EtOH}$, $[\alpha]_D^{20} +47.1^\circ$ in H_2O] as a by-product in the $\text{Ba}(\text{OBr})_2$ -oxidation of (II) and by formation of (I) from methyl-*d*-arabinofuranoside, $[\alpha]_D^{20} +123^\circ$. β -Methyl-*d*-aldohexo-(-galacto- and -gluco-)pyranosides afford a dialdehyde, $[\alpha]_D^{20} -148^\circ$ to -151° , and thence *Ba L'*-

methoxy-D-hydroxymethyldiglycollate, $+2\text{H}_2\text{O}$, $[\alpha]_D^{20} +35.9^\circ$ (corresponding acid, $[\alpha]_D^{20} +45^\circ$ in H_2O). α -Methyl-*d*-arabino- and -xylo-pyranoside give the same dialdehyde, $[\alpha]_D^{20}$ about $+125^\circ$ in H_2O , and thence *Sr* *D'*-methoxydiglycollate, $\text{Sr} \begin{array}{c} \text{O} \cdot \text{CO} \cdot \text{CH}(\text{OMe}) \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \quad \text{CH}_2 \end{array} \text{O}$, $[\alpha]_D^{20} -55.5^\circ$ in H_2O (corresponding acid, $[\alpha]_D^{20}$ about -125° in H_2O); β -methyl-*d*-arabino- and -xylo-pyranoside afford the optical antipodes thereof, characterised particularly as *Sr* *L'*-methoxydiglycollate, $[\alpha]_D^{20} +55.5^\circ$. α -Methyl-*L*-rhamnoside gives the dialdehyde, $\text{CHO} \cdot \text{CHMe} \cdot \text{O} \cdot \text{CH}(\text{OMe}) \cdot \text{CHO}$, m.p. 101—102°, $[\alpha]_D^{20} -143^\circ$ in H_2O . R. S. C.

The alkaloid of *Solanum auriculatum*, Ait. A. R. ANDERSON and L. H. BRIGGS (J.C.S., 1937, 1036—1037).—"Solanine," the gluco-alkaloid of *S. auriculatum*, is probably identical with solanine-s, from *S. sodomum* (Oddo, A., 1911, i, 670), since the aglucon prepared by hydrolysis (HCl - EtOH) yields derivatives identical with those obtained by Oddo.

J. D. R.

Pigments of cotton flowers. IV. Constitution of herbacitrin and herbacetin. K. NEELAKANTAM and T. R. SESHADRI (Proc. Indian Acad. Sci., 1937, 5, A, 357—364).—Herbacitrin (a flavonol glucoside from *Gossypium herbaceum*) (octa-acetate, m.p. 214—216°) on hydrolysis yields herbacetin, m.p. 280—283° (penta-acetate, m.p. 192—193°), and when oxidised by air in KOH yields $p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$. Its colour reactions and recent synthesis show that it is the 7-glucoside of 3:5:7:8:4'-pentahydroxyflavone. A. Lr.

Highly polymerised compounds. CLXI. Determination of the mol. wt. of polysaccharides by the terminal group method. H. STAUDINGER and E. HUSEMANN (Ber., 1937, 70, [B], 1451—1457).—Haworth's investigations in conjunction with viscosimetric and osmometric measurements indicate a thread-like form for the macromols. of cellulose whereas those of starch are extended but branched and those of glycogen are approx. spherical. The end-group method leads to a determination of mol. wt. only in the case of thread mols. Misleading results are obtained with greatly branched mols. The applicability of the method to cellulose is discussed. H. W.

Micro-modification of Pflüger's method of determining glycogen. T. VON BRAND (Skand. Arch. Physiol., 1936, 75, 195—198).—The method is based on adsorption of the glycogen (I) from alkaline solution on $\text{Zn}(\text{OH})_2$ prepared *in situ* by adding mixed aq. NaCl and ZnSO_4 . $\approx 2\text{--}3$ mg. of (I) can be determined. NUTR. ABS. (m)

Constitution of starch. I. Homogeneity of natural starch. W. S. REICH and A. F. DAMANSKY (Bull. Soc. Chim. biol., 1937, 19, 158—189; cf. A., 1933, 811, 1038).—Methods of esterifying starch are criticised on the grounds that modification in mol. structure occur. Potato starch on acetylation affords a mixture of Ac_2 (I) (82%) and Ac_3 derivative (II) (16%). Hydrolysis of (I) affords a substance similar to natural starch ("amylogen") and that of (II) a different substance ("amylon"; the "amylose" of

most authors). Acetolysis of (I) yields (II). Comparative data for benzylation and cinnamylation and also for maize starch are given. F. O. H.

Constitution of starch. II. Relationship between starch and the substances known as "amylopectin" and amylose, and the action of water on starch. W. S. REICH and A. F. DAMANSKY (Bull. Soc. Chim. biol., 1937, 19, 357—391).—The methods applied previously to potato starch are extended to the investigation of "amylopectin" and "amylose" (Ling and Nanji, J.C.S., 1923, 123, 2666). The former consists of amylogen and amylon in varying proportions depending on the method of prep.; the latter is amylon formed by hydrolysis of the amylogen. A. L.

Starch. VIII. Trimethylstarch. K. HESS and K. H. LUNG (Ber., 1937, 70, [B], 1259—1262).—Potato starch is partly methylated with NaOH and Me_2SO_4 and the product is freed from salts by thorough washing with H_2O and then by cautious treatment with light petroleum (I) and MeOAc , after which it is pptd. from solution by an excess of (I). The substance is dissolved in anisole and treated with Na in liquid NH_3 ; after removal of NH_3 , the solution is heated with MeI at 60—70°, thereby giving cryst. trimethylstarch, $[\alpha]_D^{20} +210^\circ$ in CHCl_3 , $+187^\circ$ in C_6H_6 . H. W.

Highly polymerised compounds. CLV. Constitution of glycogen. H. STAUDINGER and E. HUSEMANN (Annalen, 1937, 530, 1—20; cf. this vol., 278).—Solutions of pure P-free glycogen (I), $[\alpha]_D +200^\circ$ in $\text{HCO} \cdot \text{NH}_2$, in H_2O , CaCl_2 , and $\text{HCO} \cdot \text{NH}_2$, obey van 't Hoff's law (osmosis) and thus (I) is not a micelle-colloid. In the three solvents the degree of polymerisation is about 1750. $2N\text{-HCl}$ at 100° (2 min.) degrades (I) to a substance (II), $[\alpha]_D +200^\circ$ in $\text{HCO} \cdot \text{NH}_2$, the degree of polymerisation of which is 407—420. Fractional addition of MeOH to a $\text{HCO} \cdot \text{NH}_2$ solution of (I) gives a material (III), $[\alpha]_D +198^\circ$ in $\text{HCO} \cdot \text{NH}_2$, the degree of polymerisation of which is about 5000. $\text{C}_5\text{H}_5\text{N} \cdot \text{Ac}_2\text{O}$ gives triacetates, $[\alpha]_D +156^\circ$, $+150^\circ$, and $+160^\circ$, respectively, in CHCl_3 , of (I), (II), and (III); these esters and the glycogens recovered therefrom by hydrolysis in absence of O_2 have unchanged degree of polymerisation. These facts prove that (I) is a polymeric-homologous series of substances, which reacts as an individual in the classical sense and that the macro-mol. is a spherical colloid. η of (I), (II), and (III) are identical and very low and independent of concn. up to 5%, which confirms the spherical nature of the mol., which is shown to be hydrated ($5\text{H}_2\text{O}$ for each C_6 unit). From the above and Haworth's data it is concluded that the mol. consists of a central chain of glucosidically bound glucose units, carrying glucosidically, on $\text{C}_{(2)}$, $\text{C}_{(3)}$, and $\text{C}_{(6)}$ of each unit, chains of 12—18 glucosidically bound glucose units. In (I) the central chain contains 30—40 glucose units, in (III) a larger and in (II) a smaller no. Starch is intermediate between (I), a spherical colloid giving only sols, and cellulose, a thread colloid giving only gels. The above conception also accounts for the powdery nature of (I), its inability to swell, its low η , and obedience to the Hagen-Poiseuille law. R. S. C.

Chelation of diamines with cupric salts.—See A., I, 420.

Synthesis of spermidine and analogous triamines of the fatty series. J. VON BRAUN and W. PINKERNELLE (Ber., 1937, 70, [B], 1230—1240).—A profitable synthesis of spermidine has been realised along the lines $\text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{NHBz} \rightarrow \text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{Cl} \rightarrow \text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{NH}_2 \rightarrow \text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{NH} \cdot [\text{CH}_2]_3 \cdot \text{OPh} \rightarrow \text{NH}_2 \cdot [\text{CH}_2]_4 \cdot \text{NH} \cdot [\text{CH}_2]_3 \cdot \text{Br} \rightarrow \text{NH}_2 \cdot [\text{CH}_2]_4 \cdot \text{NH} \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$. Simplification could not be effected by use of $\text{NHBz} \cdot [\text{CH}_2]_3 \cdot \text{Br}$ or $o\text{-C}_6\text{H}_4(\text{CO}_2\text{N} \cdot [\text{CH}_2]_3 \cdot \text{Br})$ but the use of their higher homologous in the synthesis of analogous amines is very advantageous. $\text{OPh} \cdot [\text{CH}_2]_3 \cdot \text{Br}$ and benzoylputrescine (I) at 100° yield γ -phenoxypropyl- δ' -benzamido-butylamine, b.p. $235^\circ/0.4$ mm. (hydrobromide, m.p. 167° ; non-cryst. picrate; hydrochloride, m.p. 198° , best obtained from $\text{OPh} \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$ and $\text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{Cl}$ in EtOH). The base and its salts are transformed by fuming HBr at 125° into γ -bromopropylputrescine dihydrobromide, m.p. 231° (corresponding picrate, m.p. 159°), converted by prolonged action of liquid NH_3 into spermidine, $\text{NH}_2 \cdot [\text{CH}_2]_4 \cdot \text{NH} \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$, b.p. $128\text{—}130^\circ/14$ mm. (picrate, m.p. 211° ; aurichloride, m.p. 222°). Benzoylcadaverine and $\text{OPh} \cdot [\text{CH}_2]_3 \cdot \text{Br}$ afford γ -phenoxypropyl- ϵ' -benzamidoamylamine, m.p. 67° (hydrobromide, m.p. 153° ; non-cryst. picrate; hydrochloride, m.p. 180°), converted by conc. HCl at $>100^\circ$ into γ -phenoxypropylcadaverine, b.p. $155^\circ/0.4$ mm. (dihydrochloride, m.p. 265°), whence the unstable γ -bromopropylcadaverine (dihydrobromide, m.p. 203° ; picrate) and γ -aminopropyl- ϵ' -aminoamylamine (as-homospermidine), b.p. $138^\circ/14$ mm. (trihydrochloride, m.p. $223\text{—}227^\circ$; platinichloride; aurichloride, m.p. 220° ; picrate, $\text{C}_{26}\text{H}_{30}\text{O}_{21}\text{N}_{12}$, m.p. 182°). (I) and $\text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{Cl}$ give di- δ -benzamido-butylamine hydrochloride, m.p. 230° , transformed by conc. HCl at 130° into di- δ -amino-butylamine (s-homospermidine), b.p. $146^\circ/13$ mm., m.p. $16\text{—}17^\circ$ (trihydrochloride, m.p. 287° ; picrate, m.p. 249° ; aurichloride, m.p. 215°). δ -Benzamido-butyl- ϵ' -benzamidoamylamine, m.p. 136° (hydrochloride, m.p. 188°), from (I) and $\text{NHBz} \cdot [\text{CH}_2]_5 \cdot \text{Cl}$, is converted by HCl at $130\text{—}140^\circ$ into δ -aminobutyl- ϵ' -aminoamylamine, b.p. $165\text{—}166^\circ/14$ mm., m.p. 40° (trihydrochloride, m.p. 269° ; aurichloride; picrate, m.p. 192°). Di- ϵ -benzamidoamylamine, b.p. $172^\circ/14$ mm., m.p. 25° , gives a trihydrochloride, decomp. $291\text{—}293^\circ$, aurichloride, decomp. 203° , and picrate, m.p. 186° . $\text{OPh} \cdot [\text{CH}_2]_2 \cdot \text{Br}$ and EtOH- NH_3 yield $\text{NH}([\text{CH}_2]_3 \cdot \text{OPh})_2$, converted by conc. HBr at 130° into di- γ -bromopropylamine hydrobromide, m.p. 199° , which with liquid NH_3 affords di- γ -aminopropylamine, b.p. $115^\circ/14$ mm. (trihydrochloride, m.p. 254° ; aurichloride, m.p. 203° ; picrate, m.p. 230°). $\text{OPh} \cdot [\text{CH}_2]_4 \cdot \text{Br}$ and $\text{NHBz} \cdot [\text{CH}_2]_5 \cdot \text{NH}_2$ in EtOH give β -phenoxyethyl- ϵ' -benzamidoamylamine hydrobromide, m.p. 158° , in modest yield; the corresponding hydrochloride has m.p. 180° . When distilled the free base decomposes to $\text{NHBz} \cdot [\text{CH}_2]_5 \cdot \text{NH}_2$ and $\text{CH}_3 \cdot \text{CH} \cdot \text{OPh}$. The salts are transformed by HBr at 120° into β -bromoethyl- ϵ' -aminoamylamine dihydrobromide, m.p. 180° , which with liquid NH_3 affords a mixture of di- ϵ -aminoamylpiperazine and vinyl- ϵ -aminoamylamine, b.p. $85^\circ/$

12 mm., hydrogenated to ethyl- ϵ -aminoamylamine (dihydrochloride, m.p. 210°). $\text{OPh} \cdot [\text{CH}_2]_2 \cdot \text{Br}$ and $\text{NHBz} \cdot [\text{CH}_2]_4 \cdot \text{NH}_2$ yield β -phenoxyethyl- δ' -benzamido-butylamine hydrobromide (corresponding hydrochloride, m.p. 191°), which give β -phenoxyethyl- δ' -benzamido-butylamine, m.p. 58° (picrate, m.p. 112°), whence β -bromoethyl- δ' -aminobutylamine dihydrobromide, m.p. 197° , which with liquid NH_3 gives complex products and vinyl- δ -aminobutylamine, b.p. $73^\circ/13$ mm.

H. W.

Amino-alcohols derived from pentaerythritol. E. FOURNEAU, J. MATTI, and Y. DUNANT (Bull. Soc. chim., 1937, [v], 4, 1155—1157).—Compounds, $\text{OH} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{NR}_2)_3$ and $(\text{OH} \cdot \text{CH}_2)_2 \text{C}(\text{CH}_2 \cdot \text{NR}_2)_2$, are prepared from the amines and bromohydrins in C_6H_6 at $130\text{—}140^\circ$. The following are described. $\beta\beta$ -Di-(methylaminomethyl)propane- $\alpha\gamma$ -diol, m.p. 40° , b.p. $185^\circ/25$ mm. (dihydrobromide, m.p. 214° ; dihydrochloride, m.p. 198°); $\beta\beta$ -bis(dimethylaminomethyl)propane- $\alpha\gamma$ -diol, b.p. $160\text{—}162^\circ/24$ mm. (dihydrochloride, m.p. 208° , and its Bz derivative, m.p. 224°); $\beta\beta$ -bis(dimethylaminomethyl)- $\alpha\gamma$ -propylene di- α' -acetoxyphenylacetate dihydrochloride, m.p. 212° ; $\beta\beta$ -di(piperidinomethyl)propane- $\alpha\gamma$ -diol, m.p. 84° , b.p. $198^\circ/4.5$ mm. (dihydrochloride, m.p. 251°). $\beta\beta$ -Di(bromoethyl)propane- $\alpha\gamma$ -diol with NHET_2 in C_6H_6 at 118° gives $\alpha\gamma$ -epoxy- β -hydroxymethyl- β -diethylaminomethylpropane, $\text{O} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH}_2 \cdot \text{OH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{NET}_2 \end{array}$, b.p. $132^\circ/14$ mm. (hydrochloride, m.p. 135.5° , and its Bz derivative, m.p. 142°), with $\beta\beta$ -bis(diethylaminomethyl)propane- $\alpha\gamma$ -diol. $(\text{CH}_2\text{Br})_3\text{C} \cdot \text{CH}_2 \cdot \text{OH}$ and NH_2Me in C_6H_6 at 150° give the hydrobromide of $\gamma\gamma'\gamma''$ -tri(methylamino)tert.-amyl alcohol, b.p. $142^\circ/15$ mm. (hydrochloride, m.p. 229° , or, from MeOH, 155°). Tri(dimethylamino)tert.-amyl alcohol, b.p. $125^\circ/13$ mm. (trihydrochloride, m.p. 238°), is also prepared.

E. W. W.

Oxidation of hexosamines: d-glucosamine and d-glucosamic acid. R. M. HERBST (J. Biol. Chem., 1937, 119, 85—91).—Either d-glucosamine or d-glucosamic acid in aq. NaOH is oxidised by chloramine-T at 37.5° to d-arabinose and d-erythrose, with traces of HCN. Acetyl-d-glucosamine is not oxidised under these conditions.

E. W. W.

Action of diazomethane on amino-acids. R. KUHN and W. BRYDOWNA (Ber., 1937, 70, [B], 1333—1341).—Methylation is effected in homogeneous system by passing gaseous CH_2N_2 into the NH_2 -acid in H_2O . In anhyd. Et_2O most NH_2 -acids are very sparingly sol. In moist Et_2O the products resemble those obtained in H_2O . NH_2 -acids which according to measurements of dissociation and dielectric const. do not form zwitterions in H_2O give exclusively the corresponding Me esters. Conversely many NH_2 -acids which are present almost exclusively as zwitterions in H_2O afford a mixture of betaine and Me ester. The presence of zwitterions is a necessary but not sufficient condition for betaine formation with CH_2N_2 . The observations are generally explicable on the assumption that in the equilibrium, zwitterion $\rightleftharpoons \text{NH}_2$ -acid, the latter reacts with the greater rapidity with CH_2N_2 . Frequently the difference is so great that the Me ester is formed as main product when according to physical measurements

>1% of the NH_2 -acid exists as true carboxylic acid. The behaviour towards CH_2N_2 cannot be predicted from the physical consts. Thus glycine gives solely betaine whereas alanine (I) gives about equal amounts of betaine and Me ester. *l*-Leucine, *dl*-phenylalanine, *l*-proline, and *l*-hydroxyproline resemble (I). o - $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, which forms zwitterions in H_2O and can be titrated only with CH_2N_2 , gives with gaseous CH_2N_2 in H_2O 18% of anthranilbetaine and 75% of o - $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, whilst in anhyd. Et_2O the latter is formed in 97% yield. 5-Bromo-*o*-dimethylaminobenzoic acid gives 70% of the Me ester, b.p. $153^\circ/6.5\text{ mm.}$, and 20% of betaine, m.p. 130° . 2:3- $\text{NHMe}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CO}_2\text{H}$ in H_2O and Et_2O affords the corresponding Me ester. NH_2 -acids which contain comparable amounts of ion and betaine give only the corresponding Me ester (pyridine-2- and -3-carboxylic acid; *o*-, *m*-, and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$); these acids can be titrated sharply in H_2O . With aminosulphonic acids the presence of minute amounts of $\text{NH}_2\cdot\text{R}\cdot\text{SO}_3\text{H}$ causes marked electrolytic conductivity, acid reaction and titratability in H_2O . Hence a sharply titrated acid $^+\text{NH}_3\cdot\text{SO}_3^-$ gives exclusively $^+\text{NMe}_3\cdot\text{SO}_3^-$. *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ gives $^+\text{NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ and (?) the Me ester. If SO_3H is paired with a strong aliphatic NH_2 as in taurine, titratability in H_2O is lost and a complete analogy with glycine is presented and *taurobetaine* $\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3^-$ is almost quantitatively obtained. The simplest NH_2 -phenols do not give zwitterions so that the production of *o*-Me ethers is observed with *o*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, the yields being 40% and 70%, respectively; the remainder passes into brown condensation products. In anhyd. Et_2O reaction between CH_2N_2 and NH_2 -phenols is not observed.

H. W.

Action of mercuric oxide on glycine in an alkaline medium. R. TRUHAUT (Compt. rend., 1937, 204, 1348—1349; cf. A., 1933, 292).—5% glycine reduces HgO (8 mols.) in boiling *N*-NaOH with the formation of NH_3 , glycollic acid, and $\text{H}_2\text{C}_2\text{O}_4$. CO_2 , HCN , HCO_2H , and glyoxylic acid (?) are also formed.

J. L. D.

Nature of the compounds of tyrosine with polysaccharides. S. J. VON PRZYŁECKI and M. KOŁACZKOWSKA (Biochem. Z., 1937, 291, 76—78; cf. A., 1935, 1390).—The solubility of tyrosine (I) in H_2O at const. p_{H} is increased by addition of glucose, sucrose, and other sugars. The X-ray diagrams (Debye-Scherrer) of the compounds of (I) with dextrin, amylose, and starch closely resemble each other and indicate that in the compounds the (I) crystals are regularly arranged in the protein micelle.

W. McC.

Synthesis of α -amino- β -hydroxy-*n*-butyric acids. III. Simple method of preparing a mixture of the two forms. IV. Separation of mixtures of the two forms and preparation of *d*(-)- and *l*(+)-threonine. H. D. WEST and H. E. CARTER (J. Biol. Chem., 1937, 119, 103—108, 109—119).—III. In an attempt to prepare *dl*-threonine (I) [the racemic mixture of the α -amino- β -hydroxy-*n*-butyric acid from proteins (A., 1936, 1494) with its enantiomorph], crotonic acid was brominated in MeOH,

but gave only α -bromo- β -hydroxy-*n*-butyric acid-*A* [the suffix *A* is used to indicate substances related to the aminohydroxybutyric acid prepared by Abderhalden's method, as distinct from precursors of (I)]. Crotonic acid and $\text{Hg}(\text{OAc})_2\cdot\text{MeOH}$, however, give a product (reduced by H_2S to β -methoxy-*n*-butyric acid; decomp. on heating to a product, decomp. 170 — 180°), which with Br in aq. KBr (sunlight), followed by HBr, forms mixed α -bromo- β -methoxy-*n*-butyric acids, converted into mixed α -amino- β -methoxy-*n*-butyric acids (II), and thence (HBr) into mixed α -amino- β -hydroxy-*n*-butyric acids, containing 30—40% of (I).

IV. This last mixture of (I) with *dl*-allothreonine (the name now given to the *dl*- α -amino- β -hydroxy-*n*-butyric acid which does not contain the natural form) is benzoylated to *N*-benzoyl-*dl*-allothreonine (III), m.p. 175 — 176° , and *dl*-threonine (IV), m.p. 143 — 144° ; this is not, however, a satisfactory method for isolating (I). Formylation or benzoylation of the mixture (II) gives, on the other hand, readily separable formyl-*dl*-O-methyl-threonine (V), m.p. 174 — 175° , and -allothreonine, m.p. 153 — 154° , and benzoyl-*dl*-O-methyl-threonine, m.p. 158 — 159° , and -allothreonine, m.p. 129 — 130° . These compounds are hydrolysed (HBr or HCl) to *dl*-O-methyl-threonine, m.p. 215 — 218° , and -allothreonine, m.p. 230 — 233° . These are further hydrolysed (48% HBr) to *dl*-threonine, m.p. 227 — 229° , and *dl*-allothreonine, m.p. 237 — 239° , also obtained from (IV) and (III), respectively. Resolution of (V) gives formyl-*d*(-), m.p. 163 — 164° , $[\alpha]_{\text{D}}^{25} +11.8^\circ$ (brucine salt, m.p. 186 — 188° , $[\alpha]_{\text{D}}^{25} -19.4^\circ$), and formyl-*l*(+)-O-methyl-threonine, m.p. 164 — 165° , $[\alpha]_{\text{D}}^{25} -11.9^\circ$ (brucine salt, m.p. 139 — 141° , $[\alpha]_{\text{D}}^{25} -21.5^\circ$), hydrolysed to *d*(-), m.p. 214 — 216° , $[\alpha]_{\text{D}}^{25} -37.8^\circ$, and *l*(+)-O-methyl-threonine, m.p. 214 — 216° , $[\alpha]_{\text{D}}^{25} +38.2^\circ$, and thence to *d*(-)-threonine (Bz derivative; cf. A., 1936, 233), and *l*(+)-threonine, m.p. 251 — 252° , $[\alpha]_{\text{D}}^{25} +28.4^\circ$ (Bz derivative, m.p. 147 — 148° , $[\alpha]_{\text{D}}^{25} -25.5^\circ$).

E. W. W.

Fission of the disulphide linking with sodium sulphite and potassium cyanide and colorimetric determination of thiol compounds and disulphides. A. SCHÖBERL and E. LUDWIG (Ber., 1937, 70, [B], 1422—1432).—Folin's colorimetric method with $(\text{H}_2\text{O})_3\text{P}_2\text{O}_5(\text{WO}_3)_{18}$ gives accurate results with $\text{SH}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{SH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, $\text{SH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$, $\text{SH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, $\text{CO}_2\text{H}\cdot\text{CH}(\text{SH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{CHPh}\cdot\text{C}(\text{SH})\cdot\text{CO}_2\text{H}$. Rapid oxidation and constancy of colour intensity are best attained at p_{H} 5 but in practice it is necessary to await the development of max. colour in an acetate buffer. $\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is a less powerful reducing agent under these conditions but behaves normally in presence of NaHCO_3 . The presence of H_2SO_3 increases the intensity of the colour given by Folin's reaction which may become doubled in presence of much H_2SO_3 . The changes are $2\text{R}\cdot\text{SH} + (\text{H}_2\text{O})_3\text{P}_2\text{O}_5(\text{WO}_3)_{18} = \text{SR}\cdot\text{SR} + \text{H}_2\text{O} + (\text{H}_2\text{O})_3\text{P}_2\text{O}_5(\text{WO}_3)_{17}\text{WO}_2$ and $\text{SR}\cdot\text{SR} + \text{H}_2\text{SO}_3 = \text{R}\cdot\text{SH} + \text{R}\cdot\text{S}\cdot\text{SO}_3\text{H}$, which are repeated until $\text{R}\cdot\text{SH}$ is completely converted into $\text{R}\cdot\text{S}\cdot\text{SO}_3\text{H}$. It is essential for the success of the method that oxidation of $\text{R}\cdot\text{SH}$ and disproportionation of $\text{SR}\cdot\text{SR}$ occur with sufficient

rapidity. In general determinations with SO_3'' which allow measurement of very small concns. of $\text{SH}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ are as accurate as those with CN' . Quant. doubling of colour intensity is not reached with $\text{CHPh}\cdot\text{C}(\text{SH})\cdot\text{CO}_2\text{H}$, $\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, or $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, whilst the determination of $\text{SH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ and $\text{SH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ is not influenced by the presence of SO_3'' . The ready fission of the S-S linking in cystine by SO_3'' gives a simple method for its determination by means of the Pulfrich photometer. It is necessary to use a very large excess of the reagent at p_{H} about 5. Attempts to apply Folin's reagent to the determination of disulphides other than cystine were not generally successful, union of $\cdot\text{S}\cdot\text{S}\cdot$ to *sec.* and *tert.* C atoms usually causing non-reducibility. The most important source of error in the determination of SH by Na nitroprusside is the fugitive nature of the red colour. Measurements (in glycine buffer at p_{H} 10.4) must be made very rapidly. KCN stabilises the colour in a remarkable degree owing to its restriction of the oxidation of the SH-compound by O_2 . The intensity of the colour is not the same for different substrates. In the main, disulphides show the same differences in their behaviour towards KCN as towards SO_3'' . H. W.

Synthesis of cyanamide by the oxidation of glucose and ammonia. R. FOSSE and R. DE LARAMBERGUE (Compt. rend., 1937, 204, 1285—1287).—Glucose in aq. NH_3 at 75° containing KMnO_4 affords $\text{CN}\cdot\text{NH}_2$, isolated as the Ag derivative.

J. L. D.

Production of cyanamide by ammoniacal oxidation of fructose, arabinose, mannitol, and glycerol. R. DE LARAMBERGUE (Compt. rend., 1937, 204, 1431—1432).—Oxidation of these by ammoniacal KMnO_4 yields small quantities of $\text{CN}\cdot\text{NH}_2$, determined by pptn. of the Ag salt, hydrolysis to $\text{CO}(\text{NH}_2)_2$, and pptn. with xanthhydrol. A. LI.

Condensation of cyanoacetamide and formaldehyde. I. Condensation products under different conditions. T. ENKVIST (J. pr. Chem., 1937, [ii], 149, 58—64).—Equimol. amounts of $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ and CH_2O at room temp. in alkaline, aq., or dil. alcoholic solution rapidly form sol. products $\text{CN}\cdot\text{CH}(\text{CH}_2\cdot\text{OH})\cdot\text{CO}\cdot\text{NH}_2$ or $\text{CN}\cdot\text{C}(\text{CH}_2\cdot\text{OH})_2\cdot\text{CO}\cdot\text{NH}_2$ and then slowly a yellow ppt. (I), probably a mixture of $\text{C}_7\text{H}_{10}\text{O}_3\text{N}_4$ and $\text{C}_7\text{H}_7\text{O}_3\text{N}_3$ (Ag salt), which does not give an enol or biuret reaction and is not apparently affected by PCl_5 . (I) is hydrolysed by HCl to NH_4Cl , glutaric (II), and pentane- α,γ,ϵ -tricarboxylic acid. A scheme of reaction is suggested. Preservation of (I) under the mother-liquor causes its conversion into an orange-red resin (III) which becomes hard and brittle when dry; it appears to be produced by further condensation of (I) with the sol. compounds in the reaction solution. Hydrolysis of the mother-liquors from (I) gives considerable amounts of (II). During the condensation CH_2O becomes attached to N only in minor degree. The nature and amount of the products depend greatly on conditions. The condensation is accelerated by KOH and, preferably, by piperidine, which hinders the transformation of (I) into (III). H. W.

O** (A., II.)

Reduction of nitroguanidine. VIII. Formation of aminoguanidine by reduction in liquid ammonia solutions. L. P. FULLER, E. LIEBER, and G. B. L. SMITH (J. Amer. Chem. Soc., 1937, 59, 1150—1152; cf. this vol., 10).—Nitro- (I) and nitroso-guanidine are unchanged by dissolution in liquid NH_3 or $\text{NaNH}_2\cdot\text{NH}_3$; the former gives colourless, the latter yellow, solutions. When Na is added to (I) in liquid NH_3 , vigorous reaction occurs with colour changes, consumption of 3.7—4.5 Na, and formation of 10% of $\text{CN}\cdot\text{NH}_2$ (Ag₂ salt, m.p. 39.5°) and 27—30% of N_2 (probably by way of $\text{NH}_2\cdot\text{NO}_2$). However, addition of Na (6 atoms) to (I) and NH_4Cl (6 mols.) (or NaOAc) in liquid NH_3 gives 50—60% of aminoguanidine ($\text{CHPh}\cdot$ derivative, m.p. 178.5°), formed in 60—70% yield by addition of a Na- NH_4Cl mixture (6 equivs. of each) to (I) in liquid NH_3 ; this is due to NH_4^+ acting as ammoniated H^+ , and the use of liquid NH_3 as a solvent for catalytic hydrogenations is suggested. R. S. C.

Synthesis of ureides of some monobasic acids and ketones. C. E. MILLER and R. A. CAIN (J. Amer. Pharm. Assoc., 1937, 26, 418—420).—The following were prepared: α -bromohexoyl ureide, m.p. 175° , α -bromoisohexoyl ureide, m.p. 161° , and compounds, $\text{C}_7\text{H}_{12}\text{O}_2\text{N}_2\text{Br}_2$, m.p. 145° , and $\text{C}_9\text{H}_{16}\text{O}_2\text{N}_2\text{Br}_2$, m.p. 123° . F. O. H.

Synthesis of decamethylenebisguanidine (synthalin). K. S. TOPTSCHIEV and L. N. PAVLOV (Chim. Farm. Prom., 1935, No. 1, 24—25).—Sebacic acid (I) is dissolved in the picoline fraction of $\text{C}_5\text{H}_5\text{N}$ bases and treated with dry NH_3 and POCl_3 . The dinitrile of (I) is extracted from the aq. solution with C_6H_6 and after removal of solvent is distilled in a vac. The nitrile with *iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ and Na yields decamethylenediamine, which is heated with guanidine thiocyanate at 135° to form decamethylenebisguanidine (II). The product is poured into 20% aq. KOH and the dried ground material is extracted with abs. EtOH and treated with HCl to form the hydrochloride of (II). CH. ABS. (p)

Preparation and cracking of nitriles of high mol. wt. A. W. RALSTON, H. J. HARWOOD, and W. O. POOL (J. Amer. Chem. Soc., 1937, 59, 986—992).—Distillation of stear- and laur-amide at 1 atm. gives about equal amounts of acid and nitrile, formed by disproportionation of the amide to nitrile and NH_4 salt, which latter then dissociates to NH_3 and acid. Heating higher fatty acids (stearic or mixed acids from fats, oils, etc.) in a stream of NH_3 under reflux gives excellent yields of nitrile. The equilibrium, $\text{RCO}_2\text{H} + \text{NH}_3 \rightleftharpoons \text{RCO}_2\text{NH}_4$, is displaced by the excess of NH_3 ; the subsequent equilibria, $\text{RCO}_2\text{NH}_4 \rightleftharpoons \text{H}_2\text{O} + \text{RCO}\cdot\text{NH}_2 \rightleftharpoons \text{RCN} + 2\text{H}_2\text{O}$, are displaced by removal of the H_2O in the stream of NH_3 . Higher fatty acid nitriles from fats and oils are cracked by passage at 450 — 600° over catalysts (glass, pumice, Al_2O_3 on C, Al_2O_3 , or Cu or Fe on Al_2O_3), or, better, by heating alone or in N_2 at 420° , to mixed $<\text{C}_{13}$ fatty acid nitriles and saturated and unsaturated hydrocarbons; the nature of the products is investigated by hydrolysis of the nitrile, partial separation by solvents (alcohols, PhOH), and adsorption of the nitriles on to SiO_2 gel, from which they are removed

by hot H_2O . Hexo- to lauro-nitrile were identified in the products by hydrolysis to the acid and conversion into 2-alkylbenziminazoles. R. S. C.

Maleo- and fumaro-nitrile. J. JENNEN (Bull. Soc. chim. Belg., 1937, 46, 199—210).—Reaction does not occur with *trans*- C_2I_2 and KCN - EtOH or $\text{Hg}(\text{CN})_2$ whereas with CuCN at 135—200° *fumaronitrile* (I), b.p. 101°/46 mm., m.p. 96—96.4°, is obtained. Somewhat impure *cis*- C_2I_2 similarly gives (I) and *maleo-nitrile* (II), b.p. 99—99.5°/13 mm., m.p. 32.2—32.6°. Indications of the formation of (I) and (II) are not obtained when mixtures of C_2H_2 and C_2N_2 are irradiated or when C_2H_2 is passed into an irradiated solution of C_2N_2 in C_6H_6 . (I) is transformed by conc. H_2SO_4 (d 1.84) into fumardiamide whereas (II) under like conditions yields maleamic acid. Ill-defined products are obtained by the action of NaOH on (I) or (II). H. W.

Maleo- and citracono-nitrile. P. BRUYLANTS and J. JENNEN (Bull. Soc. chim. Belg., 1937, 46, 197—198).—The product (I) obtained by the action of P_2O_5 on malediamide is not identical with maleo-nitrile (II) since it is hydrolysed by NaOH to maleic acid whereas HCN is withdrawn from (II) under these conditions. (I) and (II) are transformed by conc. H_2SO_4 into maleamic acid. Fresh analyses of (I) show it to be *maleimide*. Similarly *citraconimide* is derived from P_2O_5 and citracondiamide. H. W.

Photolysis of azomethane.—See A., I, 419.

Complex compounds of bivalent platinum with glycine. A. A. GRÜNBERG and L. M. VOLSCHTEIN (Bull. Acad. Sci. U.R.S.S., 1937, 3—24).— K_2PtCl_4 and glycine (HG) yield K_2PtG_4 , from which H_2PtG_3 (I) [Ba , $(\text{NH}_4)_2$, and Ag_2 salts] is obtained with HCl or HNO_3 . (I) has markedly amphoteric properties, the series $(\text{I}) \rightarrow [\text{PtG}_3(\text{HG})]' \rightarrow [\text{PtG}_2(\text{HG})_2] \rightarrow [\text{PtG}(\text{HG})_3]' \rightarrow [\text{Pt}(\text{HG})_4]''$ being obtained by varying the p_{H} of the solutions. The salts $[\text{Pt}(\text{HG})_4]\text{X}_2$ [$\text{X}_2 = (\text{NO}_3)_2$, $[\text{PtCl}_4]$, Cl_2 , and SO_4] are prepared from (I) and the appropriate acids. (I) yields chiefly *cis*- PtG_2 with boiling H_2O , and chiefly *trans*- PtCl_2G_2 with 6*N*- HCl . The mechanism of the reactions is discussed. R. T.

Constitution, optical activity, and photochemical behaviour of platinumous complexes. III.—See A., I, 423.

Characteristic contact-catalytic transformations of cyclohexane hydrocarbons. N. I. SCHUJIKIN (J. Gen. Chem. Russ., 1937, 7, 1015—1021).—*cycloHexane* (I) yields CH_4 , C_6H_6 , and PhMe when passed over $\text{Ni-Al}_2\text{O}_3$ at 375°, in H_2 ; in presence of Pt the products are C_6H_6 and Ph_2 . *Methylcyclohexane* (II) gives *p*-xylene, C_6H_6 , and CH_4 , and *dimethylcyclohexane* gives *p*-xylene, PhMe , (I), (II), and CH_4 with $\text{Ni-Al}_2\text{O}_3$, at 330—375°. The results are explained on the basis of methylation by CH_2 radicals, and of destructive hydrogenation by H_2 . R. T.

Hydrogenation of homologues of benzene under pressure. M. K. DJAKOVA, A. V. LOZOVOR, and T. G. STEPANTZOVA (J. Gen. Chem. Russ., 1937, 7, 722—728).—Hydrogenation to alkylcyclohexanes of *PhPr*, *o*-, *m*-, and *p*-xylene, 1:2:4:5-tetra-,

penta-, and hexa-methylbenzene takes place at 200—240°/120—230 atm. (Ni catalyst) without elimination of side-chains. *Penta*-, b.p. 183—186°, and *hexa-methylcyclohexane*, b.p. 214—216°, are described. R. T.

Products of condensation of benzene with cyclohexene in presence of aluminium chloride. S. S. NAMETKIN and E. S. POKROVSKAJA (J. Gen. Chem. Russ., 1937, 7, 962—972).— C_6H_6 , *cyclohexene* (I), and AlCl_3 at 0° yield mono-, *m*- and *p*-di- (III), 1:3:5-*tri*- (IV), m.p. 65—66°, and 1:2:4:5-*tetra*- (V), m.p. 60°, -*cyclohexylbenzene*. The sole product obtained from (I) and (II) or (III) is (IV), and from (I) and (IV) is (V), showing that the process of condensation is accompanied by isomerisation. R. T.

Stable dibromide of $\Delta^{1:3}$ -cyclohexadiene. P. BEDOS and A. RUYER (Compt. rend., 1937, 204, 1350—1352).— $\Delta^{1:3}$ -*cycloHexadiene* (I) with dry HBr at -10° affords 1-bromo- Δ^2 -*cyclohexene*, b.p. 71.5°/26 mm., which with Br in dry CCl_4 at 15° gives substitution products. The Raman spectrum shows that the dibromide (II), m.p. 108°, of (I) contains a double linking, which is very inert chemically. With hot MeOH containing NaHCO_3 , (II) affords 1:4-dimethoxy- Δ^2 - and 1-bromo-2-methoxy- Δ^3 -*cyclohexene*. (II) with hot NaOH gives nearly pure *trans*-1:2-dihydroxy- Δ^3 -*cyclohexene*, m.p. 77°, whereas with hot H_2O , the *cis*-compound, an oil [*p*-nitrobenzoate, m.p. 117° and 137° (two forms)], is formed which with H_2 - Pt gives *cyclohexane*-1:2-diol. (II) with excess of aq. NaHCO_3 gives the above *cis*- and *trans*-compounds, and *cis*-1:4-dihydroxy- Δ^2 -*cyclohexene*, an oil, reduced (H_2 - Pt) to *cis*-*cyclohexane*-1:4-diol. This isomerisation leaves the structure of (II) undecided. J. L. D.

Action of nitrous anhydride on santene. A. S. ONISCHTSCHENKO (Bull. Acad. Sci. U.R.S.S., 1937, 209—223).—Santene in light petroleum and N_2O_3 yield 3-nitro-2-nitroso-2:3-dimethyl-1:4-methylenecyclohexane (I), m.p. 123—124°, converted by reduction (Sn and HCl) into 2-amino-3-hydroxy-2:3-dimethyl-1:4-methylenecyclohexane, m.p. 280—282° [*platinochloride*, m.p. 228—230° (decomp.); *aurichloride*, m.p. 186—188°]. (I) yields NO and 1:3-diacetylcyclopentane, m.p. 123—127° (*semicarbazide*, m.p. 216—217°), when warmed with EtOH . A solution of (I) in Et_2O gradually deposits 2-nitroso-3-hydroxy-2:3-dimethyl-1:4-methylenecyclohexane, m.p. 114°, on keeping. R. T.

Beryllium bromide as a reagent in syntheses. R. PAJEAU (Compt. rend., 1937, 204, 1347).— Bu^nBr with boiling PhMe containing BeBr_2 affords some PhBu^n , but the catalytic action of BeBr_2 is not general. CH_2PhCl with excess of boiling C_6H_6 containing BeBr_2 affords CH_2Ph_2 . PhMe , PhEt , and *m*-xylene react similarly. Acid chlorides do not react with C_6H_6 and BeBr_2 . J. L. D.

Reversibility of the Friedel-Crafts reaction. N. N. ORLOV and P. G. VAISFELD (J. Appl. Chem. Russ., 1937, 10, 861—868).—Products of low b.p. are not obtained from xylene and AlCl_3 at 200°, condensed rings being produced under these conditions. Addition of C_6H_6 does not favour demethylation

of xylene in presence of AlCl_3 , at the b.p., whilst addition of $\text{C}_6\text{H}_5\text{Me}_3$ leads to increased production of products of high b.p. Demethylation of xylene is achieved by heating at the b.p. with moist AlCl_3 . FeCl_3 and PCl_3 act similarly to AlCl_3 in the above reactions, but are less active. Xylene forms complexes with AlCl_3 , the activity of which is comparable with that of AlCl_3 alone. R. T.

Identification of alkylbenzenes. I. Identification of monoalkylbenzenes by means of the acetamido-derivative. V. N. IPATIEV and L. SCHMERLING (J. Amer. Chem. Soc., 1937, 59, 1056—1059).—Monoalkylbenzenes are readily identified by mono- (1:1 $\text{H}_2\text{SO}_4\text{--HNO}_3$) or di-nitration (2:1 $\text{H}_2\text{SO}_4\text{--HNO}_3$) at room temp. and conversion into the $p\text{-NHAc-}$ or 2:4-(NHAc)₂-derivatives. $\text{C}_6\text{H}_5\text{R}\cdot\text{NH}_2$ form Et_2O -sol. salts, $2\text{C}_6\text{H}_4\text{R}\cdot\text{NH}_2\cdot\text{SnCl}_2\cdot 2\text{HCl}$, readily separable from the insol. (NH_2)₂-derivatives. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$, m.p. 145°, $p\text{-ethyl-}$, m.p. 94°, $n\text{-}$, m.p. 96°, and $iso\text{-propyl-}$, m.p. 106°, $n\text{-}$, m.p. 105°, $sec\text{-}$, m.p. 126°, and $tert\text{-butyl-}$, m.p. 170°, $tert\text{-amyl-}$, m.p. 142°, and $cyclohexyl\text{-acetanilide}$, m.p. 130—131°, 2:4- $diacetamidotoluene$, m.p. 221°, $ethyl\text{-}$, m.p. 223°, $n\text{-}$, m.p. 208°, and $iso\text{-propyl-}$, m.p. 216°, $n\text{-}$, m.p. 214°, $sec\text{-}$, m.p. 192°, and $tert\text{-butyl-}$, m.p. 210°, $tert\text{-amyl-}$, m.p. 181°, and $cyclohexyl\text{-benzene}$, m.p. 261—262°, and 2:4- $diaminocyclohexylbenzene$, m.p. 105—106°, are described. Identification of PhPr^a and PhPr^b in a mixture of the two is detailed. R. S. C.

Condensation of alcohols with aromatic hydrocarbons in presence of aluminium chloride. III. Condensation of primary alcohols with benzene and toluene. I. P. TZUKERVANIK and G. VICHROVA. **IV. Condensation of aliphatic alcohols with naphthalene.** I. P. TZUKERVANIK and I. TERENTIEVA. **V. Condensation of cyclohexanol with benzene and toluene.** I. P. TZUKERVANIK and N. G. SIDOROVA (J. Gen. Chem. Russ., 1937, 7, 632—636, 637—640, 641—645).—III. $n\text{-}$ Alcohols condense with aromatic hydrocarbons at 120—124° in presence of AlCl_3 (2 mols. per mol. of alcohol), to yield alkylbenzenes. Thus C_6H_6 and EtOH (120—130°; 10 hr.) yield PhEt , $m\text{-C}_6\text{H}_4\text{Et}_2$, $\text{C}_6\text{H}_5\text{Et}_3$, $\text{C}_6\text{H}_5\text{Et}_2$, and $\text{C}_6\text{H}_4(\text{C}_6\text{H}_4\text{Et})_2$, $\text{C}_6\text{H}_5\text{Pr}^a$ and Pr^aOH (110°; 10 hr.) give PhPr^a and $m\text{-C}_6\text{H}_4\text{Pr}^a_2$, PhMe and EtOH (140°; 8 hr.) yield $m\text{-}$ and $p\text{-C}_6\text{H}_4\text{MeEt}$ and $\text{C}_6\text{H}_3\text{MeEt}_2$, and PhMe and Pr^aOH (125°; 4 hr.) afford $m\text{-}$ and $p\text{-C}_6\text{H}_4\text{MePr}^a$ and $\text{C}_6\text{H}_3\text{MePr}^a_2$.

IV. C_{10}H_8 is condensed with $n\text{-}$, $sec\text{-}$, and $tert\text{-}$ alcohols, in presence of 2, 1, and 0.5 mols. of AlCl_3 per mol. of alcohol, respectively. C_{10}H_8 and Pr^bOH in ligroin (24 hr. at room temp., and 4 hr. at 100°) give $2\text{-C}_{10}\text{H}_7\text{Pr}^b$, oxidised by 20% HNO_3 (130°; 15 hr.) to 4- $isopropylphthalic$ acid, m.p. 216° (decomp.), 2:7- $diisopropyl\text{naphthalene}$, b.p. 278—280° (*picrate*, m.p. 86°), and $\text{C}_{10}\text{H}_5\text{Pr}^b_3$, oxidised to $diisopropyl\text{phthalic}$ acid by 20% HNO_3 . C_{10}H_8 and $\text{CHMeEt}\cdot\text{OH}$ in ligroin (100°; 5 hr.) give $1\text{-C}_{10}\text{H}_7\text{CHMeEt}$ and $\text{C}_{10}\text{H}_6(\text{CHMeEt})_2$. C_{10}H_8 and Bu^nOH (100°; 3 hr.) yield 1-, b.p. 287—289° (*picrate*, m.p. 93°), and 2- $tert\text{-butyl\text{naphthalene}}$, b.p. 274—276° (*picrate*, m.p. 84—85°), and $ditert\text{-butyl\text{naphthalene}}$, m.p. 132° (*picrate*, m.p. 99°). C_{10}H_8 and $tert\text{-C}_5\text{H}_{11}\cdot\text{OH}$ (100°;

2 hr.) afford 1-, b.p. 301—303° (*picrate*, m.p. 110—113°), and 2- $tert\text{-amyl\text{naphthalene}}$, b.p. 287—290° (*picrate*, m.p. 83°), and $ditert\text{-amyl\text{naphthalene}}$, m.p. 154—155°. The side-chains of the above alkyl\text{naphthalenes} are oxidised by 5% HNO_3 (170°; 10 hr.) to yield naphthoic acids, whilst 20% HNO_3 oxidises the unsubstituted ring, to give substituted phthalic acids.

V. cycloHexanol (I) in presence of AlCl_3 (100°; 2 hr.) yields $cyclohexyl\text{-}$ (II), $m\text{-}$ and $p\text{-di-}$, and 1:3:7- $tri\text{-cyclohexylbenzene}$, m.p. 68°, with C_6H_6 , and $m\text{-}$ and $p\text{-cyclohexyl-}$, and 3:5- $dicyclohexyl\text{-toluene}$, m.p. 93.5°, with PhMe . (I) alone gives $cyclohexane$ (III) and $chlorocyclohexane$ (IV) when heated with AlCl_3 . The reaction is represented as: $(\text{I}) + \text{AlCl}_3 \rightarrow (\text{III}) + \text{AlCl}_2\cdot\text{OH} + \text{HCl}$; $(\text{III}) + \text{HCl} \rightarrow (\text{IV})$; $\text{C}_6\text{H}_6 + (\text{III}) \rightarrow (\text{II})$; $\text{C}_6\text{H}_6 + (\text{IV}) \rightarrow (\text{II}) + \text{HCl}$. R. T.

Halogenation. XVIII. Halogenation of ethylbenzene. P. S. VARMA, V. SAHAY, and B. R. SUBRAMONIUM (J. Indian Chem. Soc., 1937, 14, 157—159).— $p\text{-C}_6\text{H}_4\text{EtCl}$ is obtained in good yield by chlorinating PhEt in presence of I in the dark. Employing Br and I in a reaction medium containing $\text{NO}_2\cdot\text{SO}_3\text{H}$ there are obtained CHPhMeBr (II), $p\text{-C}_6\text{H}_4\text{BrEt}$, 2:4- $\text{C}_6\text{H}_3\text{Br}_2\text{Et}$, and $p\text{-C}_6\text{H}_4\text{IEt}$ (III). Further halogenation of (I), (II), and (III) yields 3- $bromo\text{-4-iodo-}$, m.p. 88—89°, 4- $chloro\text{-3-bromo-}$, b.p. 143—144°/10 mm., and $p\text{-chloro-}\alpha\text{-bromo-ethylbenzene}$, b.p. 120—121°/8 mm. D. J. B.

(A) Synthesis of $m\text{-}$ and $p\text{-allyl-}$ and $p\text{-propenyl-toluene}$. R. J. LEVINA. (B) Catalytic isomerisation of unsaturated hydrocarbons with a double linking in the $\alpha\beta\text{-position}$. R. J. LEVINA and D. A. PETROV (J. Gen. Chem. Russ., 1937, 7, 684—687, 747—749).—(A) $p\text{-Allyl-}$ (I) and $m\text{-allyl-}$, b.p. 60—60.5°/11 mm., and $p\text{-propenyl-toluene}$ (II) have been prepared by the Grignard reaction.

(B) (I) is converted into (II) by passing over Pt at 300° in CO_2 . $\Delta^a\text{-Butenylbenzene}$ similarly yields $\Delta^a\text{-}$ and $\Delta^b\text{-butenylbenzene}$. R. T.

Thermal polymerisation of styrene.—See A., I, 416.

Magnesium pentamethylphenyl halides. H. CLÉMENT and J. SAVARD (Compt. rend., 1937, 204, 1742—1743; cf. A., 1936, 852).— $\text{C}_6\text{Me}_5\cdot\text{MgBr}$ (I) with EtI (or EtBr) and allyl iodide affords $ethyl\text{-}$, sublimates at 118°, and $allyl\text{-pentamethylbenzene}$, sublimates at 128°, respectively. MeBr reacts but no pure compound is isolated. (I) with COMe_2 affords $pentamethylphenyldimethylcarbinol$, m.p. 134° (decomp.), easily dehydrated to $\beta\text{-pentamethylphenyl-}\beta\text{-methylethylene}$, sublimates at 122°. $\text{CH}(\text{OEt})_3$ reacts with (I) with difficulty to give $\text{C}_6\text{Me}_5\cdot\text{CHO}$.

J. L. D.

[Constitution and reactivity. XIX.] K. LAUER and R. ODA (J. pr. Chem., 1937, [ii], 148, 287—288; cf. A., 1936, 1239).—Theoretical explanations of the mode of nitration of PhNO_2 (A., 1936, 297) are revised.

R. S. C.

Action of nitrogen peroxide on benzene, toluene, or chlorobenzene. III. Nitration by means of nitrogen peroxide in presence of aluminium

chloride, PCl_3 , and mercuric nitrate. IV. Nitration by means of nitrogen peroxide of benzaldehyde and of nitro-derivatives of benzene, toluene, and chlorobenzene. A. I. TITOV (J. Gen. Chem. Russ., 1937, 7, 591—594, 667—672).—III. Nitration of C_6H_6 or PhCl by N_2O_4 at 0° in presence of anhyd. AlCl_3 proceeds: $\text{RH} + \text{N}_2\text{O}_4 + 2\text{AlCl}_3 \rightarrow \text{RNO}_2, \text{AlCl}_3$ (I) + $\text{AlCl}_2\cdot\text{OH}, \text{NOCl}$ (II) $\rightleftharpoons \text{RNO}_2, \text{AlCl}_2\cdot\text{OH} + \text{AlCl}_3, \text{NOCl}$; (I) + $\text{N}_2\text{O}_4 + \text{RH} \rightarrow \text{AlCl}_2\cdot\text{OH}, 2\text{RNO}_2, \text{NOCl}$; (II) + $\text{N}_2\text{O}_4 + \text{RH} \rightarrow \text{AlCl}(\text{OH})_2, \text{RNO}_2, 2\text{NOCl}$, or, summarily, $2\text{AlCl}_3 + 3\text{RH} + 3\text{N}_2\text{O}_4 \rightarrow 3\text{RNO}_2 + 3\text{NOCl} + \text{Al}_2\text{Cl}_3(\text{OH})_3$. Impure products are obtained in low yield when PhNO_2 , BzCl , or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ is used in place of C_6H_6 or PhCl . $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ is obtained in 50% yield when PCl_3 is substituted for AlCl_3 in the above reaction. The products obtained in presence of HgNO_3 at 0° explode when the temp. is raised to 20° .

IV. $\text{C}_6\text{H}_4(\text{NO}_2)_2, \text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2, \text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$, and $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ are obtained in good yield by nitrating the $(\text{NO}_2)_1$ -derivatives or PhCHO at 0 – 10° with N_2O_4 in oleum. Alternatively, 35% oleum containing 30% of N_2O_4 is added to PhNO_2 at 70° , followed by $\text{K}_2\text{S}_2\text{O}_8$; the reactions are: $\text{RH} + \text{N}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{RNO}_2 + \text{NO}\cdot\text{HSO}_4 + \text{H}_2\text{O}$; $\text{RH} + \text{NO}\cdot\text{HSO}_4 + \text{K}_2\text{S}_2\text{O}_8 \rightarrow \text{RNO}_2 + \text{H}_2\text{SO}_4 + \text{SO}_3 + \text{K}_2\text{SO}_4$.

R. T.

Bromination of 4-diphenyl benzenesulphonate. S. E. HAZLET (J. Amer. Chem. Soc., 1937, 59, 1087—1088).—Although $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{OH}$ gives 3-bromo-4-hydroxydiphenyl (PhSO_2 derivative, m.p. 102—103°), $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{O}\cdot\text{SO}_2\text{Ph}$ gives 4'-bromo-4-diphenyl benzenesulphonate, m.p. 79—81°, hydrolysed to and also prepared from 4-bromo-4'-hydroxydiphenyl.

R. S. C.

Sulphonation by means of sulphites. I. Mechanism of the Piria reaction. S. V. BOGDANOV and S. A. CHEIFETZ (J. Gen. Chem. Russ., 1937, 7, 911—916).— PhNO_2 or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ and aq. NaHSO_3 or Na_2SO_3 yield mixtures of sulphimino-benzenesulphonic acid and sulphimino-benzene (or -toluene), the proportion of the former rising with increasing alkalinity of the solution. NO-compounds are supposed to be intermediate products in both cases.

R. T.

Halogenation. XVII. Bromination and iodination of diphenyl. P. S. VARMA and M. KRISHNAMURTI (J. Indian Chem. Soc., 1937, 14, 156).—Bromination of Ph_2 in presence of CCl_4 , NaNO_2 , and oleum gives 2:2'- and 4:4'-($\text{C}_6\text{H}_4\text{Br}$) $_2$. With I and $\text{NO}_2\cdot\text{SO}_3\text{H}$ 4:4'-di-iododiphenyl, m.p. 202°, is obtained.

D. J. B.

Mesitylene derivatives. II. Derivatives of di-2:4:6-trimethylphenylmethane (dimesitylmethane). W. T. NAUTA and P. J. WUIS (Rec. trav. chim., 1937, 56, 535—540).—Passage of dry HCl into a boiling C_6H_6 solution of dimesitylcarbinol (I) (Kohler *et al.*, A., 1932, 1250) affords dimesitylmethyl chloride (II), m.p. 104—105°, converted by heating with $\text{N}\cdot\text{KOH}\cdot\text{EtOH}$ into dimesitylmethyl ether (III), m.p. 61°, and by AgOAc into dimesitylmethyl acetate (IV), m.p. 98°. Boiling MeOH converts either (II) or (IV) into (III). The conductivity (Λ_{191} 3.82; Λ_{199} 10.7) of (II) in liquid SO_2 at -10°

is intermediate between that of CHPh_2Cl ($\Lambda_{20.3}$ 0.005) and $(p\text{-OMe}\cdot\text{C}_6\text{H}_4)_2\text{CHCl}$ ($\Lambda_{26.79}$ 4.84) and CPh_3Cl ($\Lambda_{20.8}$ 7.70). (II) gives evidence of free radical formation when it is treated with Ag in C_6H_6 (O_2 exclusion). (III) and (IV) also give coloured solutions in liquid SO_2 and possess small conductivity but (I) gives a colourless, non-conducting solution.

J. W. B.

cis-trans Isomerisation by bromine atoms. M. S. KHARASCH, J. Y. MANSFIELD, and F. R. MAYO (J. Amer. Chem. Soc., 1937, 59, 1155).—*iso*Stilbene in C_6H_6 is stable in the dark or in light in the presence of HBr and antioxidants, in the dark in the presence of HBr alone in air or vac., but is isomerised to stilbene by HBr in light (more rapidly in air) or in the presence of peroxides in the dark. $\text{Br}\cdot\text{HBr}$ in the dark and HCl under any conditions do not cause isomerisation, which is thus considered to be caused by Br atoms.

R. S. C.

Synthesis of optically-active molecules with the aid of circularly polarised light. G. KARAGUNIS and G. DRIKOS (Praktika, 9, 177—181; Chem. Zentr., 1936, i, 3298).—Irradiation of asymmetrical triarylmethyl radicals with circularly polarised light in the presence of Cl_2 or Br yields optically active products, right-polarised light giving *l*-materials and *vice versa*. No activity is observed with symmetrical radicals or with ordinary light; control experiments show that the reaction is an asymmetric synthesis, not an asymmetric decomp. It is concluded that triarylmethyl radicals have a tetrahedral configuration.

H. N. R.

Radical containing three triphenylmethyl groups. E. CONNERADE (Bull. Soc. chim. Belg., 1937, 46, 179—193).— $\text{CO}(\text{C}_6\text{H}_4\text{Bz}\cdot p)_2$ is converted by LiPh into *di*-4:4'-hydroxybenzhydryltriphenylmethylcarbinol (I), $\text{OH}\cdot\text{CPh}(\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH})_2$, m.p. 104—105° after becoming vitreous at 98°, decomp. 180—200°, less readily obtained by use of MgPhBr or from $\text{CO}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}\cdot p)_2$. (I) in CHCl_3 is transformed by HCl and ultimately by SOCl_2 into *di*-4:4'-chlorobenzhydryltriphenylmethyl chloride, m.p. 160—161° (slight decomp.) after becoming darker at 141°, the solution of which in boiling C_6H_6 is reduced by Ag powder to the triradical (II), $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2$. Treatment of (II) in C_6H_6 with air cause colour change from red-violet to orange-red and addition of light petroleum ppts. the triperoxide, $(\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2)_2$, m.p. 165°, and then a mixture of the dimeric monoperoxide diquinone and dimeric diperoxide monoquinone. (II) is rapidly transformed by Br into *di*-4:4'-bromobenzhydryltriphenylmethyl bromide.

H. W.

Cracking of decahydroanthracene in presence of anhydrous aluminium chloride. R. J. LEVINA, J. K. JURIEV, and A. I. LOSCHKOMONIKOV (J. Gen. Chem. Russ., 1937, 7, 1005—1008).—The products contain aromatic 16—24, naphthenic 64—76%, and traces of aliphatic hydrocarbons.

R. T.

Dissociable organic oxides. Action of oxidising agents on meso-diphenylanthracene: two stereoisomeric meso-dihydroxides. C. DUFRAISSE

and J. LE BRAS (Bull. Soc. chim., 1937, [v], 4, 1037—1045).—An improved prep. of 9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene (I) is described (cf. A., 1932, 507). Simultaneously an *isomeride* (II), m.p. 185° and after solidification 195—196°, is formed in small (0.25—0.5%) yield. Diphenylanthracene with KMnO_4 in C_6H_6 -aq. H_2SO_4 below 8° affords (II) in 75% yield under carefully controlled conditions. With KI in AcOH, (II) and (I) afford *meso*-diphenylanthracene (III), which with CrO_3 in aq. AcOH at 20° affords mainly (I), but some (II). In the absence of H_2O , $\text{o-C}_6\text{H}_4\text{Bz}_2$ is formed, whereas 18% HNO_3 affords some (I) but mostly gums. Attempts to reduce (I) and (II) to the monoxide were unsuccessful (cf. A., 1931, 1052). An explanation is advanced in the light of Baeyer's strain theory. J. L. D.

Photo-sensitive nitro-compounds. III. *meso*-Nitroanthracenemonosulphonic acids. IV. Action of light on nitro-sulphonic acids in water, or on wool or paper. N. N. VOROSCHCOV and V. V. KOZLOV (J. Gen. Chem. Russ., 1937, 7, 729—738, 996—1004).—III. Anthracene-1-sulphonic acid in AcOH and HNO_3 (2—3 days at room temp.) yield 9-nitroanthracene-1-sulphonic acid (I) (Na , $+\text{H}_2\text{O}$; Ca , $+\text{2H}_2\text{O}$; Ba , $+\text{3H}_2\text{O}$; Cu^{II} , $+\text{3H}_2\text{O}$; Hg^{I} , $+\text{2H}_2\text{O}$; Hg^{II} , $+\text{3H}_2\text{O}$; Fe^{III} , $+\text{2H}_2\text{O}$; Pb , $+\text{6H}_2\text{O}$; Ag , $+\text{2H}_2\text{O}$ salts); sulphonation of 9-nitroanthracene was unsuccessful. (I) is reduced to the 9- NH_2 -derivative (II) by Zn in H_2SO_4 at 95°, the product of diazotisation of which does not yield the expected sultone with boiling H_2O . The sultone, m.p. 156—159°, of (II) is obtained by heating (II) with POCl_3 (130°; 3 hr.), and yields 9-hydroxyanthracene-1-sulphonic acid when hydrolysed with 5% NaOH . An attempt at determining the position of the NO_2 -group of *meso*-nitroanthracene-2-sulphonic acid (Cu^{II} , $+\text{3H}_2\text{O}$; Ba , $+\text{H}_2\text{O}$; Pb , $+\frac{1}{2}\text{H}_2\text{O}$; Fe^{II} , $+\text{4H}_2\text{O}$; Ag salts) was not successful. (I) exhibits considerable photo-sensitivity.

IV. The effect of light on the coloration of a no. of nitro-sulphonic acids and their salts has been studied. R. T.

10-Substituted 1:2-benzanthracene derivatives. L. F. FRESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1937, 59, 1028—1036).—10-Substituted derivatives of 1:2-benzanthracene and its 7-OMe-derivative are obtained in good yield (with, in some cases, by-products) from the benz-10-anthrone. The latter compounds must be pure, since they decompose readily if impure; satisfactory syntheses are described. The 1:2-benz-10-anthranol-anthrone equilibrium lies more to the anthranol side than in the unsubstituted anthrone series.

$\text{o-CO}_2\text{H-C}_6\text{H}_4\text{-CO-C}_{10}\text{H}_7$ - α (I), m.p. 174—176°, obtained pure only with much loss by the Friedel-Crafts reaction in $\text{C}_2\text{H}_2\text{Cl}_4$, is best (75%) prepared from $1\text{-C}_{10}\text{H}_7\text{-MgBr}$ and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$, and with Zn-NaOH gives a 20% or with $\text{H}_2\text{-Cu}$ chromite at 175°/102—156 atm. (no reduction in EtOH) gives an 82% yield of $\text{o-}\alpha$ -naphthylmethylbenzoic acid (II), m.p. 148—148.5°; if prepared by the Friedel-Crafts reaction, (I) gives a mixture with the β -isomeride,

which is difficultly separable; if prepared from crude $1\text{-C}_{10}\text{H}_7\text{Br}$, (I) contains sufficient Br-acid (derived from $\text{C}_{10}\text{H}_6\text{Br}_2$) as impurity to inactivate the Cu chromite by reduction to the metal by HBr. With $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ at 20—30° (II) gives 94% of crude 1:2-benz-10-anthrone (III), m.p. 130—135°, which decomposes when kept and is unsuitable for further work; $\text{H}_2\text{SO}_4\text{-AcOH}$ at 50—60° gives crude 1:2-benzanthryl 10-acetate (IV), m.p. 152—154°, and some (III); 0.1 mol. of ZnCl_2 in boiling $\text{AcOH-Ac}_2\text{O}$ (3:2) gives a 91% yield of pure (IV), m.p. 163—163.5° (softens at 161°), which with $\text{MgBu}^{\text{a}}\text{Br}$ gives 84% of yellow 1:2-benz-10-anthranol (V), m.p. 154.5—155.5° (fluorescent; colourless COMe_2 compound), obtained less well by hydrolysis by HCl-MeOH . Isomerisation of (V), best in COMe_2 , is accompanied by decomp., but gives pure (III), m.p. 180—181° (decomp.) (not fluorescent; yellow). 10-Methoxy-1:2-benzanthracene, m.p. 110.5—111°, is best (55%) obtained by interaction of (IV) with $\text{MgBu}^{\text{a}}\text{Br}$ in Et_2O , heating with Me_2SO_4 in PhMe, and removing (V) and more oxygenated compounds by adsorption on Al_2O_3 . By isomerising pure (V) in hot PhMe and adding MgRX to the equilibrium mixture are obtained 10-ethyl-, m.p. 113.5—114° (picrate, m.p. 141—141.5°), 10-n-propyl- (VI), m.p. 107—108° [picrate, m.p. 126.5—127.5°; with some 1:2-benzanthracene (VII)], 10-allyl-, m.p. 125.5—126.5° [picrate, m.p. 132—133°; hydrogenated to give (VI)], 10-n-butyl-, m.p. 96.8—97.5° (picrate, m.p. 115—115.5°), and 10-n-amy-1:2-benzanthracene, m.p. 82.5—83.5° [picrate, m.p. 111—111.5°; with some of the compound (VIII), $\text{C}_{36}\text{H}_{24}\text{O}_2$, m.p. 265—267° (decomp.)]; $\text{MgPr}^{\text{a}}\text{Cl}$, however, gives 10-isopropyltetrahydro-1:2-benzanthracene, m.p. 72.5—73.5° (picrate, m.p. 134.5—135.5°), which with Se at 300—305° gives (VII), but at 240—245° gives 10-isopropyl-1:2-benzanthracene, m.p. 93—93.5° (picrate, m.p. 159—160°). Cyclisation of $\text{o-4'-methoxy-1'-naphthylmethylbenzoic acid}$ at 3—5° gives 35% of pure 3-methoxy-1:2-benz-10-anthrone (IX), m.p. 183—184°, and a mixture thereof with the corresponding anthranol, m.p. 192—193°, the latter being also derived by the action of $\text{C}_6\text{H}_5\text{N}$ on (IX) with some of the condensation product, $\text{C}_{38}\text{H}_{28}\text{O}_4$, m.p. 268—275° (decomp.), analogous to (VIII). Action of MgRX on (IX) gives good yields of 3-methoxy-10-methyl-, m.p. 183—183.5° (dipicrate, m.p. 149—150°), -ethyl-, m.p. 161—161.5° (dipicrate, m.p. 143.5—144°), and -n-propyl-1:2-benzanthracene, m.p. 136—136.5° (dipicrate m.p. 140—140.5°); the 10-Me compound with HBr-AcOH gives 3-hydroxy-10-methyl-1:2-benzanthracene, m.p. 193—194° (decomp.). M.p. are corr.

R. S. C.

Catalytic oxidation of alicyclic amines with the side-chain $\text{CH}_2\text{-NH}_2$. I, II. Z. I. SCHUJKINA (J. Gen. Chem. Russ., 1937, 7, 983—988, 989—993).—I. Aq. aminomethylcyclopropane, O_2 , and Cu or OsO_4 give cyclopropanaldehyde (oxime, m.p. 86°; phenylhydrazone, m.p. 67°), which with dimedon yields cyclopropyl-2:6-diketo-4:4'-dimethylcyclohexyl-2'-hydroxy-6'-keto-4':4'-dimethyl- Δ^1 -cyclohexenylmethane, m.p. 168°, and with MeNO_2 and K_2CO_3 gives α -hydroxy-

β -nitroethylcyclopropane, reduced by Sn and HCl to α -hydroxy- β -aminoethylcyclopropane (platinichloride).

II. $\text{NH}_2\cdot\text{CH}_2\text{R}$ (I) ($\text{R} = \text{cyclobutyl}$), Cu, and O_2 yield $\text{R}\cdot\text{CHO}$ (II), which condenses with (I) to a Schiff's base, $\text{CHR}\cdot\text{N}\cdot\text{CH}_2\text{R}$, b.p. $88-90^\circ/15$ mm. This, when distilled from aq. $\text{H}_2\text{C}_2\text{O}_4$, regenerates (II), which undergoes a Cannizzaro reaction, giving $\text{R}\cdot\text{CO}_2\text{CH}_2\text{R}$. Cryst. products are not formed with NH_2OH or $\text{NHPH}\cdot\text{NH}_2$ and (II), which gives a compound, m.p. 154° , analogous to that with cyclopropanaldehyde. R. T.

Pterotactic derivatives of bivalent platinum with optically active, cyclic *trans*-1 : 2-diamines.—See A., I, 423.

Benzylation of aromatic amines. V. Reactions between *o*-, *m*-, and *p*-cyanobenzyl chlorides and aniline, ethylaniline, and dimethylaniline. D. H. PEACOCK, and P. THA (J.C.S., 1937, 955).—Velocity coeffs. of the above reactions are tabulated; *m*- reacts faster than *p*-cyanobenzyl chloride, CN thus resembling NO_2 . Introduction of CN lowers rate of reaction. *o*-Cyanobenzyl chloride reacts more slowly than CH_2PhCl ; with NH_2Ph it is fastest, with NPhMe_2 slowest, of the three CN-compounds. E. W. W.

Aromatic compounds of fluorine. XXII. Question of an *ortho*-effect. G. SCHIEMANN and H. G. BAUMGARTEN (Ber., 1937, 70, [B], 1416—1422).—Chlorination of *o*- $\text{C}_6\text{H}_4\text{MeF}$ under defined conditions gives *o*-fluorobenzotrichloride (I), b.p. $94.6^\circ/12$ mm., *o*-fluorobenzylidene chloride, b.p. $71.6^\circ/13$ mm., or *o*-fluorobenzyl chloride, b.p. $86^\circ/38$ mm. (I) is transformed by CaCO_3 and boiling H_2O into *o*- $\text{C}_6\text{H}_4\text{F}\cdot\text{CO}_2\text{H}$ (II), m.p. 126° . Treatment of (II) in conc. H_2SO_4 with HN_3 in CHCl_3 at 0° and subsequently at $65-70^\circ$ does not give *o*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$ whereas *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$ and NH_2Ph are readily obtained under similar conditions from *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{CO}_2\text{H}$ and BzOH , respectively. *o*- $\text{C}_6\text{H}_4\text{F}\cdot\text{CO}\cdot\text{NH}_2$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling H_2O yield *o*-fluorobenzhydrazide, m.p. 70° , whence the non-cryst. azide (*s*-di-*o*-fluorophenylcarbamide, m.p. 226°) and *o*-fluorophenylurethane which could not be converted into *o*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$; this could not be obtained from *o*- $\text{C}_6\text{H}_4\text{F}\cdot\text{CO}\cdot\text{NH}_2$ and NaOBr . *o*-Fluorobenzchloroamide, m.p. $87-88^\circ$, is converted by $\text{Ba}(\text{OH})_2$ and steam into *o*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$ in 89% yield. H. W.

Preparation of methylethylaniline. J. J. MAKAROV-ZEMLIANSKI (J. Appl. Chem. Russ., 1937, 10, 660—670).— NPhMeEt is obtained in 90% yield from $\text{NHPH}\cdot\text{Et}$ and Me_2SO_4 , MeHSO_4 and MeOH , or MeOH and H_2SO_4 , at $170-240^\circ$. R. T.

Homologues of *o*-nitrophenylhydroxylamine. R. KUHN, H. VETTER, and P. DESNUELLE (Ber., 1937, 70, [B], 1314—1318).—The homologues of *o*-nitrophenylhydroxylamine are much more stable than the parent substance and can be preserved unchanged for months in an evacuated desiccator. They give dark violet primary alkali salts and are converted by conc. NaOH into brown or yellowish-brown secondary salts which are readily hydrolysed by H_2O . 3-Nitro-2-amino-5 : 6 : 7 : 8-tetrahydronaphthalene is converted by $\text{K}_2\text{S}_2\text{O}_8$ in conc. H_2SO_4 into 3-nitro-2-nitroso-5 : 6 : 7 : 8-tetrahydronaphthal-

ene, decomp. 153° , oxidised to 2 : 3-dinitro-5 : 6 : 7 : 8-tetrahydronaphthalene, m.p. 107.5° , and reduced by ascorbic acid in $\text{EtOH}\cdot\text{H}_2\text{O}$ to 3-nitro-2-hydroxylamino-5 : 6 : 7 : 8-tetrahydronaphthalene, m.p. 125° . 6-Nitro-5-nitrosohydriindene, m.p. $155-156^\circ$, is oxidised to 5 : 6-dinitrohydriindene, m.p. $111-112^\circ$, and reduced to 6-nitro-5-hydroxylaminohydriindene, m.p. 117° (decomp.). 4-Nitro-5-hydroxylamino-*o*-xylene has m.p. 88° (decomp.). 4-Nitro-5-nitroso-*m*-xylene is reduced to 4-nitro-5-hydroxylamino-*m*-xylene, m.p. 87° (decomp.). H. W.

Tenacity of organic radicals. X. J. VON BRAUN, R. MICHAELIS, and H. SPÄNIG (Ber., 1937, 70, [B], 1241—1249; cf. A., 1933, 1285).—The firmness of union of $\cdot\text{CH}_2\text{Ph}$ to N is most appreciably increased by the introduction of $\cdot\text{NO}_2$, to a smaller extent by $\cdot\text{CN}$, and to a minor degree by $\cdot\text{NHAc}$, the effect of which is similar to that of halogen (except F). The three firmly attached $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ residues show little differences among themselves; the more mobile $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ groups are similar only in the two firmly attached groups (*o* and *m*), whereas among the labile $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ groups a distinct differentiation is observed according to the position of the substituent. The amines $\text{CH}_2\text{R}'\cdot\text{NMe}\cdot\text{CH}_2\text{R}''$ are obtained by warming $\text{CH}_2\text{R}'\text{Cl}$ or $\text{CH}_2\text{R}'\text{Br}$ (1 mol.) with a *sec.* base $\text{NHMe}\cdot\text{CH}_2\text{R}''$ (2 mols.) derived from $\text{CH}_2\text{R}''\text{Cl}(\text{Br})$ with excess of NH_2Me in C_6H_6 . Treatment with CNBr occurs at 0° and finally at 100° . The product is dissolved in Et_2O , shaken with dil. H_2SO_4 and the bromide and cyanamide are separated from one another by fractional distillation. The following substances are new : *m*-nitrobenzylmethylamine, b.p. $118^\circ/0.3$ mm. (hydrochloride, m.p. 191° ; picrate, m.p. 160°); di-*m*-nitrobenzylmethylamine, b.p. $230^\circ/0.3$ mm., m.p. 80° ; benzyl-*p*-nitrobenzylmethylamine, b.p. $221^\circ/12$ mm. (hydrochloride, m.p. 172° ; methiodide, m.p. 173°); *p*-nitrobenzylmethylcyanamide, b.p. $190^\circ/0.5$ mm.; *p*-chlorobenzyl-*p'*-nitrobenzylmethylamine, b.p. $200^\circ/0.3$ mm. (hydrochloride; picrate, m.p. 166°); *p*-chlorobenzyl bromide, b.p. $119^\circ/12$ mm., m.p. 48° ; *m*-chlorobenzyl-*p'*-nitrobenzylmethylamine, b.p. $224^\circ/0.5$ mm. (hydrochloride, m.p. 181° ; methiodide, m.p. 179°); *m*-chlorobenzyl chloride, b.p. $120^\circ/14$ mm.; *o*-chlorobenzyl-*p'*-nitrobenzylmethylamine, b.p. $234^\circ/0.5$ mm.; *p*-chlorobenzyl-*m'*-nitrobenzylmethylamine, b.p. $220^\circ/0.3$ mm. (hydrochloride, m.p. 188° ; picrate, decomp. 56°); *m*-nitrobenzylmethylcyanamide, b.p. $168-170^\circ/0.5$ mm.; *o*-chlorobenzyl-*o'*-nitrobenzylmethylamine, b.p. $178-180^\circ/0.3$ mm. (hydrochloride, m.p. 152° ; picrate, decomp. 68°); *o*-nitrobenzylmethylcyanamide, b.p. $173-175^\circ/0.3$ mm.; *m*-nitrobenzyl-*p'*-nitrobenzylmethylamine, b.p. $232-234^\circ/0.3$ mm. (hydrochloride, m.p. 229° ; picrate, m.p. 160°); *o*-nitrobenzyl-*m'*-nitrobenzylmethylamine, b.p. $220^\circ/0.5$ mm., m.p. 86° (hygroscopic hydrochloride; picrate, m.p. 161° ; methiodide, m.p. 137°); *o*-iodobenzyl-*o'*-nitrobenzylmethylamine, b.p. $205^\circ/0.5$ mm., m.p. $40-42^\circ$ (hydrochloride, m.p. 157° ; picrate, m.p. 118°); *p*-cyanobenzylmethylamine, b.p. $148-151^\circ/14$ mm.; di-*p*-cyanobenzylmethylamine, b.p. $212-215^\circ/14$ mm.; *m*-cyanobenzylmethylamine, b.p. $144-145^\circ/14$ mm. (hydrochloride, m.p. 155°); benzyl-*p*-cyanobenzylmethylamine, b.p. $220-224^\circ/11$ mm. (non-cryst.

picrate; methiodide, m.p. 198°); *p*-cyanobenzylmethylcyanamide, b.p. 145°/0.2 mm.; *o*-iodobenzyl-*p*-cyanobenzylmethylamine, b.p. 258—260°/14 mm. (non-cryst. picrate; methiodide, m.p. 220°); *o*-iodobenzyl bromide, b.p. 118—120°/0.5 mm., m.p. 56°; *p*-cyanobenzylmethylcyanamide, b.p. 150°/0.3 mm.; *p*-nitrobenzyl-*p*'-cyanobenzylmethylamine, b.p. 197—199°/12 mm. (methiodide, m.p. 210°); *p*-cyanobenzyl bromide, b.p. 141—143°/12 mm., m.p. 115°; *p*-nitrobenzylmethylcyanamide, b.p. 178—180°/12 mm.; *m*-cyano-*p*-benzyl-*p*'-cyanobenzylmethylamine, b.p. 252—254°/14 mm. (non-cryst. picrate; methiodide, m.p. 262°); *o*-cyanobenzyl-*m*'-cyanobenzylmethylamine, b.p. 216—218°/0.2 mm. (non-cryst. picrate; methiodide, m.p. 198°); benzyl-*p*-aminobenzylmethylamine, b.p. 164—167°/0.4 mm., m.p. 48°; benzyl-*p*-acetamidobenzylmethylamine, m.p. 104°; *p*-acetamidobenzylmethylcyanamide, m.p. 108°; *p*-chlorobenzyl-*p*'-aminobenzylmethylamine, b.p. 200°/0.4 mm. (picrate, m.p. 102°); *p*-chlorobenzyl-*p*'-acetamidobenzylmethylamine (not volatile without decomp.; non-cryst.) (picrate, m.p. 124°); *o*-iodobenzyl-*p*'-nitrobenzylmethylamine, m.p. 104° (picrate, m.p. 191°); *o*-iodobenzyl-*p*'-aminobenzylmethylamine, b.p. 210—212°/0.5 mm. (hygroscopic hydrochloride, m.p. 200°); non-cryst. *o*-iodobenzyl-*p*'-acetamidobenzylmethylamine; *p*-acetamidobenzyl bromide, b.p. 130—132°/0.2 mm.; *o*-iodobenzylmethylcyanamide, b.p. 205—208°/12 mm.; *o*-nitrobenzyl-*p*'-nitrobenzylmethylamine, b.p. 226—230°/0.3 mm. (picrate, m.p. 140°); *o*-aminobenzyl-*p*'-aminobenzylmethylamine, b.p. 186—188°/0.5 mm., m.p. 60° (picrate, m.p. 112°); *o*-acetamidobenzyl-*p*'-acetamidobenzylmethylamine, b.p. 226—228°/0.3 mm.; *o*-aminobenzylmethylamine, b.p. 133—137°/11 mm. [hydrochloride, m.p. 218°, also obtained by reduction of *o*-nitrobenzylmethylamine, b.p. 138—140°/12 mm. (hydrochloride, m.p. 175°)]; *o*-aminobenzyl-*m*'-aminobenzylmethylamine, b.p. 188—190°/0.3 mm., m.p. 58°; *o*-acetamidobenzyl-*m*'-acetamidobenzylmethylamine, b.p. 220—225°/0.2 mm. (picrate, m.p. 95°).

H. W.

Nitration and halogenation of $\alpha\beta$ -dianilinoethane and its derivatives. I. A. E. SCHOUTEN (Rec. trav. chim., 1937, 56, 541—561).—(CH_2NHPH_2)₂ (I) with HNO_3 (*d* 1.52) at -10° gives $\alpha\beta$ -di-(2:4:6-trinitrophenylnitroamino)ethane, named "ditetrayl," the structure of which is proved by its similar formation from $\alpha\beta$ -di-*o*- and -*p*-nitro- (*Ac* derivative, m.p. 217°), -2:4-dinitro- (*Ac* derivative, m.p. 234°), and -2:4:6-trinitro- (*Ac* derivative, m.p. 242°) -anilinoethane, and by the formation of picric acid when hydrolysed by NaOH. Exactly similar series of reactions are carried out with various halogeno-derivatives of (I), the following data being new: *o*-C₆H₄Cl·NH₂ and (·CH₂Br)₂ with NaOAc at 150° afford $\alpha\beta$ -di-*o*-chloroanilinoethane, m.p. 67° (*Ac* derivative, m.p. 118°), nitrated to give $\alpha\beta$ -di-(2-chloro-4:6-dinitrophenylnitroamino)ethane (II), m.p. 238°. 1:2:4-C₆H₃Cl₂·NO₂ with (·CH₂·NH₂)₂·H₂O·EtOH at 150° gives $\alpha\beta$ -di-2-chloro-4-nitroanilinoethane, m.p. 308° (*Ac* derivative, m.p. 232°); the corresponding 4:6-(NO₂)₂ compound, m.p. 172° (*Ac* derivative, 293°), is similarly prepared from 2-chloro-4:6-dinitroaniline, m.p. 36°, (lit. amorphous). Nitration of either gives (II). Similarly are obtained $\alpha\beta$ -di-*o*-

bromoanilinoethane, m.p. 76° (*Ac* derivative, m.p. 192°), and its 4-NO₂-, m.p. 318° (*Ac* derivative, m.p. 264°), and 4:6-(NO₂)₂-derivative, m.p. 156° (*Ac* derivative, m.p. 308°), whence $\alpha\beta$ -di-(2-bromo-4:6-dinitrophenylnitroamino)ethane, m.p. 240°, is obtained: $\alpha\beta$ -di-*p*-chloroanilinoethane, m.p. 99° (*Ac* derivative, m.p. 138°), its 2-NO₂-, m.p. 253° (*Ac* derivative, m.p. 265°), and 2:6-(NO₂)₂-derivative, m.p. 222° (*Ac* derivative, m.p. 248°), and $\alpha\beta$ -di-(4-chloro-2:6-dinitrophenylnitroamino)ethane, m.p. 203°; $\alpha\beta$ -di-*p*-bromoanilinoethane, m.p. 108° (*Ac* derivative, m.p. 158°), its 2-NO₂-, m.p. 247° (*Ac* derivative, m.p. 281°), and 2:6-(NO₂)₂-derivative, m.p. 199° (*Ac* derivative, m.p. 225°); $\alpha\beta$ -di-(4-bromo-2:6-dinitrophenylnitroamino)ethane, m.p. 205°, and $\alpha\beta$ -di-(2:6-dinitro-*p*-tolylnitroamino)ethane, m.p. 229°. The *Ac*₁, m.p. 235°, and *Ac*₂ derivative, m.p. 110°, of 2-bromo-4:6-dinitroaniline are described. J. W. B.

Constitution of double salts. XX. Diammines with benzidine and tolidine. G. SPACU and C. G. MACAROVICI (Bul. Soc. Stiinte Cluj, 1935, 8, 286—295; Chem. Zentr., 1936, i, 3446).—By the action of tolidine (Tld) and benzidine (Bzd) on the double salts CdCl₂·2NiCl₂·12H₂O, CdCl₂·CuCl₂·4H₂O, and HgCl₂·CoCl₂·4H₂O, the following compounds are obtained: [CdCl₆][NiBzd₂]₂; [CdCl₆][MnBzd₂][CdBzd₂]; [CdCl₆][CuBzd₂]; [CdCl₆][CuTld₂]; [HgCl₆][CoTld₂]. By the action of NH₃ on [CdCl₆][Cu(C₅H₅N)₄], [CdCl₆][Cu(NH₃)₄] is formed. J. S. A.

Preparation of soluble aromatic amido-compounds of therapeutic value.—See B., 1937, 620.

Azo-indicators with a quaternary ammonium group. G. S. HARTLEY (J.C.S., 1937, 1026—1029).—For use as acidimetric indicators in aq. solutions containing long paraffin chain cations etc., colour-ions with resultant positive charge in both acid and alkaline form are prepared. *p*-NO₂·C₆H₄·CH₂Cl and NMe₃ yield *p*-nitrobenzyltrimethylammonium chloride (iodide also prepared), reduced to the *p*-NH₂-compound. This when diazotised couples with amines to give azo-compounds, viz., with NHMe₂ (iodide), α -C₁₀H₇·NH₂, α -C₁₀H₇·NMe₂, and β -C₁₀H₇·NH₂; these are indicators, changing from yellow (alkaline) to red at *p*_H 3.3, 4.5, 4.5, and 1.3, respectively. A compound with α -C₁₀H₇·OH, changing from red (alkaline) to orange-yellow at *p*_H 8.5, is also prepared. E. W. W.

Reaction between *p*-hydroxyazobenzene and organo-magnesium compounds. A. TAURINS (J. pr. Chem., 1937, [ii], 149, 1—29).—Gradual addition of a dil. solution of a suitable Grignard reagent to a dil. solution of *p*-OH·C₆H₄·N₂·Ph does not cause evolution of a hydrocarbon and results in the separation of additive compounds (I) Mg(R···OH·C₆H₄·N·NPh)₂·MgX₂·4Et₂O. Such compounds have been obtained with MgEtBr, MgEtI, MgPr^oBr, MgPr^oI, and MgPhBr. Sol. compounds appear to arise with MgPr^oCl and MgBu^oCl. If solutions of the Grignard reagent and *p*-OH·C₆H₄·N₂·Ph (1:1) are rapidly mixed, one-half of the expected vol. of hydrocarbon is evolved and additive compounds (II), NPh·N·C₆H₄·O·Mg·R···OH·C₆H₄·N·NPh·MgX₂·4Et₂O, are pptd. These are observed with MgMeI, MgEtI,

MgPr^aI, CH₃Ph·MgCl, MgPhBr, and α-C₁₀H₇·MgBr. (I) and (II) lose Et₂O when kept in open vessels whereby the red-brown colour of (I) passes into the red-violet of (II). Treatment of *p*-OH·C₆H₄·N₂·Ph with a large excess of MgMeI, MgEtCl, MgEtBr, MgEtI, MgPr^aCl, MgPr^aBr, MgPr^aI, MgBu^aCl, MgBu^aBr, MgBu^aI, or MgPhBr causes reduction to NH₂Ph and *p*-NH₂·C₆H₄·OH with evolution of saturated (III) and unsaturated (IV) hydrocarbons. The ratio of (III) to (IV) suggests the schemes $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OMgBr} + 2\text{MgEtBr} \rightarrow \text{MgBr} \cdot \text{NPh} \cdot \text{N}(\text{MgBr}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMgBr}$ (V) + 2C₂H₅; (V) + 2MgEtBr → NPh(MgBr)₂ + (MgBr)₂N·C₆H₄·OMgBr + 2C₂H₅; 4C₂H₅ → 2C₂H₄ + 2C₂H₆ except in the case of MgMeI. MgEt₂, MgPr^a₂, and MgBu^a₂ react at approx. the same rate with *p*-OH·C₆H₄·N₂·Ph and give about the same amounts of reaction products. Their reaction appears similar to that of the Mg alkyl bromides with the same alkyl radical. H. W.

Action of bases on nitrophenylhydrazines. II. A. K. MACBETH and J. R. PRICE (J.C.S., 1937, 982—984).—In the reaction between NaOH, KOH, or Ba(OH)₂ with 2 : 4-dinitrophenylhydrazine, at 20°, or at 60°, to give *m*-C₆H₄(NO₂)₂ (I), *mm'*-dinitroazoxybenzene (II), and 6-nitro-1-hydroxy-1 : 2 : 3-benzotriazole (III) (cf. A., 1934, 1344), the amount of (III) is independent of the cation present, and is a min. for a certain concn. of alkali, with corresponding max. for (I) and (II). Among the products from 1 : 2 : 4-C₆H₃Cl(NO₂)₂ and N₂H₄, the supposed dinitroazonaphthalene (A., 1926, 163) is 4 : 4'-dinitro-2 : 2'-azoxynaphthalene, m.p. 305—306°. E. W. W.

Decomposition of fluorene- and fluorenone-2-diazonium chloride in acetic acid. H. V. CLABORN and H. L. HALLER (J. Amer. Chem. Soc., 1937, 59, 1055—1056).—Fluorene-2-diazonium chloride in H₂O gives 2-hydroxyfluorene (I) [Ac derivative (II), m.p. 128°]; in glacial AcOH it gives 46.7% of (II), 11% of (I), and 10% of 2-chlorofluorene. Fluorenone-2-diazonium chloride in H₂O gives 55% and in dil. AcOH 80% of 2-hydroxyfluorenone and in glacial AcOH 60% of 2-acetoxyfluorenone, m.p. 157°. R. S. C.

Equimolar condensations of aldehydes with phenols. Preparation of primary saturated phenols. J. B. NIEDERL, Y. NIEDERL, S. SHAPIRO, and M. E. MCGREAL (J. Amer. Chem. Soc., 1937, 59, 1113—1115).—1 mol. each of phenols and aldehydes in AcOH-HCl at -5° give polymeric alkylphenols, which, when slowly pyrolysed, give alkylphenols. Thus are obtained *p*-C₆H₄Et·OH, b.p. 210—212° (90°), 2-, b.p. 223—228° (125°), and 3-methyl-4-ethyl-, b.p. 230—235° (131°), 4-methyl-2-ethyl-phenol, b.p. 215—221° (133°), *p*-*n*-propyl-, b.p. 228—230° (86°), -*n*-, b.p. 238—242° (81°), and -*iso*-butyl-, b.p. 235—239° (124—125°), -*n*-amyl-, b.p. 248—253° (90°), and -*n*-heptyl-phenol, b.p. 271—278° (94°), the figures in parentheses being the m.p. of the corresponding aryloxyacetic acids. PhOH and CH₂O give a cresol in small yield. *n*, *d*, and PhOH coeff. of the alkylphenols are recorded. R. S. C.

Preparation of thymol from *m*-cresol. V. Action of phosphoric acid, zinc chloride, and the

Niederl reagent on thymol isopropyl ether. K. ONO and M. IMOTO (J. Soc. Chem. Ind. Japan, 1936, 39, 483—484B; cf. this vol., 58).—Thymol Pr^a ether with H₃PO₄ or ZnCl₂ at 190—200° affords about equal amounts of 6-isopropyl-*m*-tolyl Pr^a ether and thymol and with AcOH-H₂SO₄ much (?) 4 : 6-diisopropyl-*m*-cresol and a little thymol. R. F. P.

Preparation of thymol from *m*-cresol. VI. Action of phosphoric acid and of zinc chloride on *m*-tolyl isopropyl ether in presence of isopropyl alcohol. VII. Decomposition of isopropyl ethers of *m*-cresol and its homologues by Grignard reagents. K. ONO and M. IMOTO (J. Soc. Chem. Ind. Japan, 1937, 40, 90B).—VI. Treatment of *m*-C₆H₄Me·OPr^a (I) with Pr^aOH and H₃PO₄ at 160—170° affords (in low yield) a mixture of 1 : 4 : 3- (II) and 1 : 2 : 5-C₆H₃MePr^a·OPr^a (III); the major portion of (I) is recovered. (I) with ZnCl₂ under reflux affords a mixture of (II), (III), the corresponding phenols, and possibly 5-methyl-2 : 4-diisopropylphenyl Pr^a ether, b.p. 265—270°.

VII. It is stated (no experimental data) that *m*-C₆H₄Me·OPr^a and (II) are converted by Grignard reagents into *m*-cresol and thymol, respectively.

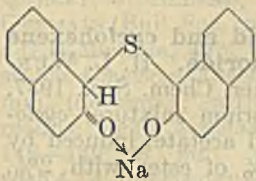
P. G. C.

Migration reactions in polycyclic systems. II. Fries rearrangement of 4-acetoxydiphenyl. K. H. CHEETHAM and D. H. HEX (J.C.S., 1937, 770—772; cf. A., 1936, 991; this vol., 23).—With AlCl₃, 4-acetoxydiphenyl gives, with some 4-hydroxydiphenyl, 4-hydroxy-3-acetyldiphenyl (cf. A., 1936, 1374; 4-OMe-derivative). This is converted by NaOAc-Ac₂O into 3-acetyl-6-phenyl-2-methylchromone (I), m.p. 143.5°, and by Na-EtOAc into the Na salt of 3-acetoacetyl-4-hydroxydiphenyl, which with AcOH-HCl yields 6-phenyl-2-methylchromone (II), m.p. 163.5°. With PhCHO, (II) forms 6-phenyl-2-styrylchromone, m.p. 202.5°. Both (I) and (II) are hydrolysed to 4-hydroxydiphenyl-3-carboxylic acid. E. W. W.

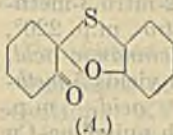
Derivatives of the hydroxydiphenyls. III. 4-Nitro-3-hydroxydiphenyl. J. C. COLBERT, W. MEIGS, and R. L. JENKINS (J. Amer. Chem. Soc., 1937, 59, 1122—1124; cf. A., 1934, 1345).—*m*-C₆H₄Ph·OH and 1 mol. of HNO₃ in AcOH at 10—15° give amongst oily products 4-nitro-3-hydroxydiphenyl, m.p. 103.1—103.3° (*x*-Br-derivative, m.p. 109°), the structure of which is proved by its formation also from *p*-C₆H₄Ph·NO₂ and KOH in C₆H₆ at 72—76°; excess of HNO₃ gives 2 : 4-dinitro-3-hydroxydiphenyl, m.p. 172.5—173° (also obtained from the 4-NO₂-compound), the structure assigned being based on lack of reactivity. Br gives only oils, unless <3 mols. are used, when (?) 2 : 4 : 6-tribromo-3-hydroxydiphenyl, m.p. 92°, is formed. 2 : 4-Di-, m.p. 100°, 2 : 4 : 6'-tri-, m.p. 131°, and 2 : 4 : 6-trinitro-3'-phenyldiphenyl ether, m.p. 143°, are described. R. S. C.

Covalent alkaline derivatives of di-2-hydroxy-1-naphthyl sulphide and of di-2-hydroxy-1-naphthylmethane. W. J. EVANS and S. SMILES (J.C.S., 1937, 727—730).—Di-2-hydroxy-1-naphthyl sulphide (I) in 5% NaOH gives the Na derivative

(+4H₂O), m.p. 255°. This, being highly sol. in Et₂O, is regarded as having the annexed structure (without resonance). With MeI-MeOH it gives the Me ether of (I) (cf. A., 1931, 723), and with NaOMe-MeI-MeOH, the Me₂ ether (J.C.S., 1913, 103, 345). The *Li* (+4H₂O and +2H₂O), no m.p., *K* (+2H₂O), m.p. 230°, and *Rb* (+2H₂O), m.p. 212°, compounds are obtained similarly. Di-3-bromo-2-hydroxy-1-naphthyl sulphide gives a *Na* derivative (+2H₂O), m.p. 300°. Di-2-hydroxy-1-naphthylmethane (II) gives *Na* (+4H₂O), m.p. 255° [converted by MeI or Me₂SO₄ into the *Me* ether of (II), m.p. 142° (*Ac* derivative, m.p. 131–133°, also obtained from di-2-methoxy-1-naphthylmethane and Ac₂O)], *Li* (+4H₂O), no m.p., and *K* (+2H₂O), m.p. 245°, derivatives, and the compound C₂₁H₁₅O₂K, C₂₁H₁₆O₂, 2H₂O, m.p. 170°. E. W. W.



stituted di-*o*-hydroxyphenyl sulphides are also prepared, and, by the action of K₃Fe(CN)₆, their dehydroderivatives, in conformation and extension of the work of Lesser and Gad (A., 1923, i, 561), whose formulæ for the latter are corr. to the basic structure (A).



5-Chloro-*o*-cresol 3-sulphide has m.p. 145°. 5-Chloro-*p*-2-xylenol 3-sulphide forms a dehydro-compound, m.p. 165°, and a *Na* derivative (+4H₂O), m.p. 155°; ψ -cuminol sulphide a dehydro-compound, m.p. 97°, and a *Na* derivative (+4H₂O), m.p. 245°. The *Na* derivative of 2-chloro-*m*-5-xylenol 6-sulphide loses H₂O when heated, and passes into the electrovalent state (no m.p.). All sulphides which furnish dehydro-compounds are either derivatives of β -naphthol 2-sulphide, or, if derived from 2 : 2'-dihydroxydiphenyl sulphide, contain the 6-Me group, which is also necessary for the formation of a covalent Na derivative. The formation of both thus depends on the possibility of a hydroxy-ketonic structure being formed.

E. W. W.

Rearrangement of *o*-hydroxy-sulphones. VI. C. S. McCLEMENT and S. SMILES (J.C.S., 1937, 1016–1021).—Certain substituted *o*-hydroxyphenyl-*o'*-nitrophenyl sulphones are converted by NaOH into *o*-*o'*-nitrophenoxysulphinic acids, characterised by conversion into sulphones and by elimination of the SO₂H. The sulphones are prepared by H₂O₂-AcOH oxidation of the corresponding sulphides, derived from 2-nitrophenylchlorothiol and the appropriate phenol. The following are described. 2'-Nitro-2-hydroxy-3 : 5 : 6-trimethyldiphenyl sulphone (I), m.p. 177°; 5-chloro-2'-nitro-2-hydroxy-3 : 6-dimethyldiphenyl sulphide, m.p. 191°, and sulphone (II), m.p. 164°; 3-chloro-2'-nitro-2-hydroxy-5 : 6-dimethyldiphenyl sulphide, m.p. 189°, and sulphone (III), m.p. 177°; 3-chloro-2'-nitro-2-hydroxy-4 : 6-dimethyldiphenylsulphone (IV), m.p. 164°; 5-chloro-2'-nitro-2-hydroxy-3-methyldiphenyl sulphide, m.p. 139°, and sulphone (V), m.p. 159°; 3-chloro-2'-nitro-2-hydroxy-5-methyldiphenyl sulphide, m.p. 142° (best from 2-nitrophenyl-4'-hydroxy-*m*-tolyl sulphide and SO₂Cl₂ in CHCl₃), and sulphone (VI), m.p. 198°; and 3-chloro-2'-nitro-2-hydroxy-4 : 5-dimethyldiphenyl sulphide, m.p. 152° (by action of SO₂Cl₂ on 2'-nitro-2-hydroxy-4 : 5-dimethyldiphenyl sulphide, m.p. 157°, from *o*-4-xylenol), and sulphone (VII), m.p. 155°. With 2*N*-NaOH, the following are obtained, at varying rates, and are degraded by HgCl₂ followed by EtOH-HCl to the ethers mentioned. From (I), 2'-nitro-6-methylsulphonyl-2 : 4 : 5-trimethyldiphenyl ether, m.p. 146° (giving 2'-nitro-2 : 4 : 5-trimethyldiphenyl ether, m.p. 80°); from (II), 5-chloro-2-*o*-nitrophenoxy-3 : 6-dimethylbenzenesulphinic acid, m.p. 125° (methylsulphone, m.p. 148°; 4-chloro-2'-nitro-2 : 5-dimethyldiphenyl ether, m.p. 70°); from (III), a sulphinic acid giving 2-chloro-2'-nitro-6-methylsulphonyl-3 : 5-dimethyldiphenyl ether, m.p. 71°; from (IV), 4-chloro-2'-nitro-6-methylsulphonyl-3 : 5-dimethyldiphenyl ether, m.p. 113° (disulphide, m.p. 142°; 4-chloro-2'-nitro-3 : 5-dimethyldiphenyl ether, m.p. 64°); from (V), 4-chloro-2'-nitro-2-methyldiphenyl ether, m.p. 39°; from (VI), 2-chloro-2'-nitro-4-methyldiphenyl ether m.p. 57°; and from (VII), 2-chloro-2'-nitro-3 : 4-dimethyldiphenyl ether, m.p. 115°. The above ethers are also synthesised directly (cf. A., 1927, 660). Sub-

Syntheses in the phenanthrene series. VII.

5 : 9-Dimethoxy- and 5-methoxy-1-methylphenanthrene. P. HILL, W. F. SHORT, and H. STROMBERG (J.C.S., 1937, 937–941).—1 : 5-C₁₀H₆(OMe)₂ (I) with succinic anhydride (II) and AlCl₃ in PhNO₂ or CS₂ gives β -(4 : 8-dimethoxy-1-naphthoyl)propionic acid (III), m.p. 173.5–174° (*Me* ester, m.p. 91–92°), also obtained from the Mg derivative of 4 : 1 : 5-C₁₀H₅Br(OMe)₂ and (II). In C₂H₂Cl₄, (I) and (II) with AlCl₃ give β -(4-hydroxy-8-methoxy-1-naphthoyl)propionic acid, m.p. 184°, methylated to (III). Zn or Cu-Zn in aq. NaOH-NH₃ does not reduce (III), which with Zn-Hg in AcOH-HCl, followed by MeOH-HCl, yields the *Me* ester, m.p. 67–67.5°, of γ -(4 : 8-dimethoxy-1-naphthyl)butyric acid (IV), m.p. 154° (yield 20%), with (I). P₂O₅ in C₆H₆ converts (IV) into 1-keto-5 : 9-dimethoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene, m.p. 124° [2 : 4-dinitrophenylhydrazones, m.p. 295° (decomp.)], which with MeMgI gives 5 : 9-dimethoxy-1-methyl-3 : 4-dihydrophenanthrene, m.p. 111–111.5°, dehydrogenated (Pd-C) to 5 : 9-dimethoxy-1-methylphenanthrene, m.p. 139–140° (*picrate*, m.p. 200°), oxidation of which gives red amorphous products from which 5-methoxy-1-methylphenanthra-9 : 10-quinone could not be isolated. 1 : 5-OMe-C₁₀H₆-OH (V), CH₂:CH-CH₂Br, and K₂CO₃ in COMe₂ give 5-methoxy- α -naphthyl allyl ether, m.p. 103°, which at 240°/22 mm. yields 5-methoxy-2-allyl- α -naphthol (VI), m.p. 82–83°. This with Me₂SO₄ in Claisen's KOH gives 1 : 5-dimethoxy-2-allylnaphthalene, m.p. 24–25°, oxidised (KMnO₄) to 1 : 5-dimethoxy-2-naphthoic acid. With C₂H₅N, HCl at 220° (N₂), (VI) gives 5-methoxy-1-methyl-1 : 2-dihydro- α -naphthofuran, m.p. 116°. With KHCO₃ at 220°, (V) gives 1-hydroxy-5-methoxy-2-naphthoic acid (VII), m.p. 212.5–213° (*Me* ester, m.p. 118–119°), which with CH₂N₂ yields the *Me* ester, m.p. 80–81°, of 1 : 5-dimethoxy-2-naphthoic acid, m.p. 151–152°, hydrolysed to (VII). Alternatively (VII) is prepared by oxidation of 1 : 5-dimethoxy-2-naphthaldehyde. 4 : 1 : 5-C₁₀H₅Br(OMe)₂ yields (Grignard and CO₂) 4 : 8-dimethoxy-1-naphthoic acid, m.p. 222.5° (*Me* ester, m.p. 173–173.5°), also obtained by methylation of 4 : 8-dihydroxy-1-naphth-

aldehyde (VIII) to the Me_2 ether, m.p. 131—131.5°, oxidised to the acid. With KOH at 180—200° (VIII) gives 4:8-dihydroxy-1-naphthoic acid, m.p. 213°. *o*-Allyltoluene is oxidised to *o*-tolylacetic acid. A reproducible method of nitrating $m\text{-OMe}\cdot C_6H_4\cdot CHO$ is described. K *o*-tolylacetate and 2-nitro-3-methoxybenzaldehyde, with Ac_2O , give 2-nitro-, m.p. 220°, reduced to 2-amino-3-methoxy- α -*o*-tolylcinnamic acid, m.p. 205—206°, which when diazotised yields 5-methoxy-1-methylphenanthrene-10-carboxylic acid, m.p. 224—225°. The last when heated with quinoline-Cu gives 5-methoxy-1-methylphenanthrene, m.p. 76—77° (picrate, m.p. 180—181°). E. W. W.

Manufacture of condensation products from hydroxy- and amino-derivatives of pyrene and chrysene.—See B., 1937, 527.

Manufacture of alkylphenols and related compounds.—See B., 1937, 528.

Manufacture of hydroarylated aromatic hydroxy-compounds.—See B., 1937, 358.

Oxidation of quinol in air in presence of *n*-butylammonium sulphite. (MLLE.) Y. GARREAU (Compt. rend., 1937, 204, 1570—1572; cf. this vol., 66, 251).—When quinol is stirred in aq. solution containing NH_4Bu^+ (236 g.), SO_2 65 g., and $Cu(OH)_2$ 4.5 g. per litre, different products are obtained according to the concn. of quinol used. With 0.2 mol. of quinol per litre after 8 days, butylammonium α -2:5-dibutylamino-1:4-benzoquinone-monosulphonate (I), m.p. 150° (hydrolysed immediately by dil. HCl to 2:5-di-*n*-butylamino-1:4-benzoquinone), and butylammonium 2:5-dibutylamino-1:4-benzoquinone-3:6-disulphonate (II), m.p. 200—205°, are formed. With quinol (0.5 mol.), a β -form, m.p. 215° (+ H_2O), of (I) (converted by dil. HCl into the corresponding acid) is formed together with butylammonium 2:5-dihydroxy-1:4-benzoquinone-3:6-disulphonate, m.p. 220—225°, which may result from the decomp. of (II). J. L. D.

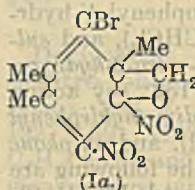
2:7:2':7'-Tetrahydroxy-1:1'-dinaphthyl. K. BRASS and R. PATZELT (Ber., 1937, 70, [B], 1341—1348).—2:7- $C_{10}H_6(OH)_2$ is oxidised by $FeCl_3$ under exactly defined conditions to 2:2':7:7'-tetrahydroxy-1:1'-dinaphthyl (I), m.p. 214° (also + H_2O , softens at 150—152°, and + $2H_2O$, m.p. 114°). All forms of (I) become discoloured when preserved in substance or in boiling H_2O but the change does not appear deep-seated. When heated at about 300° (I) gives 2:7- $C_{10}H_6(OH)_2$. (I) is converted by boiling $AcOH\text{-}Ac_2O\text{-}NaOAc$ into a tetra-acetate, m.p. 184°, by $BzCl$ and 25% KOH into a tetrabenzoate, m.p. 242.5°, and by $Me_2SO_4\text{-}NaOH$ in boiling MeOH into a Me_2 ether, m.p. 150°. $p\text{-NO}_2\cdot C_6H_4\cdot N_2Cl$ and (I) in alkaline solution give 8-*p*-nitrobenzeneazo-2:2':7:7'-tetrahydroxy-1:1'-dinaphthyl or the di-*p*-nitrobenzeneazo-compound if a large excess of the reagent is used. Distillation of (I) with Zn dust affords $C_{10}H_8$ and perylene (II) but not dinaphthyl (III) which, moreover, is not an intermediate in the formation of $C_{10}H_8$ and (II). Under similar conditions 3:3':4:4'-tetrahydroxydinaphthyl or its Ac_4 derivative gives $C_{10}H_8$ and (III) but not (II). H. W.

Preparation of alkylcyclohexanols.—See B., 1937, 529.

Condensation of acetic acid and cyclohexene in the presence of boron fluoride. H. L. WUNDERLY and F. J. SOWA (J. Amer. Chem. Soc., 1937, 59, 1010—1011).—The equilibrium mixture, cyclohexene + $AcOH \rightleftharpoons$ cyclohexyl acetate, induced by BF_3 at 80° contains 8.1—8.8% of ester with 2%, 23.5—23.8% with 4%, and about 31% with 6—18% of BF_3 ; with $\leq 15\%$ of BF_3 the % of ester decreases slowly with time. The ester dissolves 1 mol. of BF_3 and the low yield of ester with small amounts of catalyst is due to removal of the latter. The peculiar conditions of the above apparent equilibrium are due to the combined results of truly reversible esterification, irreversible polymerisation by higher concns. of BF_3 , and reversible removal of BF_3 . R. S. C.

Application of Curtius reaction to the synthesis of β -methoxy- β -phenylethylamine hydrochloride. P. P. T. SAH and C. Z. TSEU (J. Chinese Chem. Soc., 1937, 5, 134—139).—Me cinnamate and $Hg(OAc)_2$ yield Me α -(acetatomercuri)- β -methoxy- β -phenylpropionate, m.p. 140°, decomposed by $NH_3\text{-}H_2S$ to Me β -methoxy- β -phenylpropionate. This ester gives (N_2H_4) the hydrazide, m.p. 145—147° ($m\text{-NO}_2\cdot C_6H_4\cdot CHO$ derivative, m.p. 192°), of β -methoxy- β -phenylpropionic acid, which through the azide forms the urethane, m.p. 68—69°, hydrolysed (HCl) to β -methoxy- β -phenylethylamine hydrochloride, m.p. 157—159°. F. R. S.

Polymethylbenzenes. XVIII. Action of nitric acid on bromodurene. L. I. SMITH, F. L. TAYLOR, and (Miss) I. M. WEBSTER (J. Amer. Chem. Soc., 1937, 59, 1082—1086).—The compound (I), $C_{10}H_{11}O_5N_2Br$, obtained from bromodurene by fuming HNO_3 (cf. Smith *et al.*, A., 1935, 1114), is shown by the following reactions and those described previously to be probably 3-bromo-6-nitro-2:4:5-trimethylbenzyl nitrate or possibly (Ia). CH_2O (guaiacol colour reaction only) is probably formed, as well as 2-bromo-5:6-dinitro-1:3:4-trimethylbenzene, by the action of conc. H_2SO_4 on (I). H_2SO_4 in aq. $AcOH$ converts (I) into 3-bromo-6-nitro-2:4:5-trimethylbenzyl alcohol (II), m.p. 188°, with HNO_3 and a trace of HNO_2 , and H_2SO_4 in Ac_2O gives the acetate, m.p. 86°, of (II), also obtained by acetylation of (II) and readily hydrolysed to it by $HCl\text{-}EtOH$. HNO_3 (*d* 1.5) and (II) at 0° give (I). $HCl\text{-}EtOH$ converts (I) into the chloride, m.p. 112.5—113.5°, of (II), which, however, cannot be obtained directly from (II) and resists hydrolysis, but with NaI in $COMe_2$ gives the iodide, m.p. 113—115°, converted by $AgNO_3$ in hot dioxan into (I). $NaOEt$ converts (I) into 3-bromo-6-nitro-2:4:5-trimethylbenzaldehyde, m.p. 193°, sensitive to light and $KOH\text{-}H_2O\text{-}COMe_2$. Oxidation of (I) is slow and gives indefinite material. Durylaldehyde with Br in H_2SO_4 gives (?) α :2:5-tribromoduryl 2:5-dibromodurylate, m.p. 219—220°, and with $KNO_3\text{-}H_2SO_4$ at -8° gives a substance, m.p. 139—140°, which resists Br . R. S. C.



Synthesis of methoxybenzyl alcohols. R. QUELET, J. ALLARD, J. DUCASSE, and (Mlle.) Y. GERMAIN (Bull. Soc. chim., [v], 1937, 4, 1092—1101).—*o*-C₆H₄Me·OMe, 40% CH₂O, and HCl yield very unstable 4-methoxy-3-methylbenzyl chloride, b.p. 119°/12 mm. (decomp.); with NaOAc the crude substance readily yields 4-methoxy-3-methylbenzyl alcohol, b.p. 148—149°/18 mm. (phenylurethane, m.p. 90·5°), with 4:4'-dimethoxy-3:3'-dimethyldiphenylmethane. Similarly *m*-C₆H₄Me·OMe gives, after treatment of the chloride, 4-methoxy-2-methylbenzyl alcohol, m.p. 143—147°/18 mm. (phenylurethane, m.p. 71°), with 4:4'-dimethoxy-2:2'-dimethyldiphenylmethane. *p*-C₆H₄Me·OMe gives (ZnCl₂) 2-methoxy-5-methylbenzyl chloride, b.p. 124°/16 mm., which with NaOAc-AcOH gives the acetate, b.p. 146°/16 mm., of 2-methoxy-5-methylbenzyl alcohol, b.p. 140—141°/16 mm. (phenylurethane, m.p. 90°). 2:4:1-OMe·C₆H₃MePr⁶ gives 4-methoxy-2-methyl-5-isopropyl-benzyl chloride, b.p. 148°/16 mm., of which the crude product is converted into the -benzyl alcohol, new m.p. 35° (phenylurethane, m.p. 101°), with 4:4'-dimethoxy-2:2'-dimethyl-5:5'-diisopropyl-diphenylmethane, m.p. 73°, b.p. 225—230°/16 mm., oxidised to the corresponding benzophenone, m.p. 139°. *o*-NO₂·C₆H₄·OMe gives (ZnCl₂) 3-nitro-4-methoxybenzyl chloride, m.p. 85·5—86°, converted into the acetate, m.p. 37°, of 3-nitro-4-methoxybenzyl alcohol. The above benzyl alcohols are all oxidised (KMnO₄) to the corresponding benzoic acids. E. W. W.

Oxidation of ergosterol-B₃. Y. H. CHEN (Ber., 1937, 70, [B], 1432—1437).—Ergosteryl-B₃ acetate, m.p. 132°, [α]_D²⁰ -183·5°, is oxidised by Pb(OAc)₄ in AcOH to ergostadienetriol triacetate (I), C₂₈H₄₃O₃Ac₃, m.p. 172—173°, [α]_D²⁰ +14·3° in CHCl₃, hydrolysed by KOH-EtOH to ergostadienetriol, m.p. 227°, converted by boiling Ac₂O partly into (I) but mainly into acetylergostadienone (II), C₃₀H₄₆O₃, m.p. 180—181°, [α]_D¹⁹ +36·5° in CHCl₃, which does not afford a semicarbazone and is converted by NaOAc, Ac₂O, and Zn dust into a substance, C₃₂H₅₀O₄, m.p. 168°. Hydrogenation (Pt-sponge in AcOH) of (II) yields acetyl-ergostanol, m.p. 144—145°. Ozonisation of (I) affords $\alpha\beta$ -dimethylbutaldehyde. H. W.

Thermal decomposition of α -tocopherol. E. FERNHOLZ (J. Amer. Chem. Soc., 1937, 59, 1154—1155).— α -Tocopherol is probably a mono-ether of duroquinol, since at 350° it decomposes to this quinol and an oil. R. S. C.

Constituents of senega root. I. α -Spinasterol. J. C. E. SIMPSON (J.C.S., 1937, 730—733; cf. A., 1932, 381; 1935, 210).— α -Spinasterol (I) (isolated from senega root as the benzoate), new [α]_D¹⁷ -3·7° (all rotations in CHCl₃), is oxidised (CrO₃-AcOH) to α -spinastadienone (II), m.p. 176—176·5°, [α]_D¹⁷ +19·5° (oxime, m.p. 253—255°). Its Ac derivative (III) gives with BzO₂H in CHCl₃ α -spinasteryl acetate oxide, m.p. 158·5—159°, [α]_D¹⁷ +1·4°, converted by MeOH-KOH into α -spinasterol oxide, m.p. 165°, also obtained from (I). (III) is oxidised (CrO₃-AcOH) to an acetate, C₃₀H₄₆O₃ or C₃₀H₄₈O₃, m.p. 211—213·5° (converted by NH₂OH into a product, m.p. 191—193°, and by EtOH-KOH into an alcohol, C₂₈H₄₄O₂ or C₂₈H₄₆O₂, m.p. 151—152°), with a substance, C₃₀H₄₆O₄ or

C₃₀H₄₈O₄, m.p. 170—171°. (I) is unchanged by maleic anhydride, and thus lacks conjugated ethylenic linkings. It is regarded as a tetracyclic sterol, not containing a 5:6-double linking [since it has not high laevorotation, and since (II) shows only slight absorption at 2520 and 2440 Å., and not at 2450 Å.]. E. W. W.

Properties of calciferol.—See A., III, 327.

Influence of solvent on the course of chemical reactions. XV. Aromatic monocarboxylic acids. K. LAUER (Ber., 1937, 70, [B], 1288—1293).—The product of the dissociation const. of BzOH, 1- and 2-C₁₀H₇·CO₂H, and anthracene-1-, -2-, and -9-carboxylic acid and the squares of the dipole moment of the corresponding Me esters is not const. as with phenols; the same holds for the product, dissociation const. \times sp. exaltation of the Et esters. The divergence is shown particularly by carboxylic acids having a *peri* H atom; in these there is present a six-membered, subsidiary valency ring in which only one ion participates, thereby raising the electrolytic dissociation const. This view is in harmony with the observation that the α -hydroxyanthraquinones which contain a similar ring involving both ions have a remarkably small dissociation const. H. W.

Isomorphism of organic compounds. II. H. LETTRÉ, H. BARNBECK, W. FUHST, and F. HARDT (Ber., 1937, 70, [B], 1410—1416).—Isomorphism among *o*-, *m*-, and *p*-OH·C₆H₄·CO₂H, -C₆H₄Cl(Br)·CO₂H, and -C₆H₄Me·CO₂H has been investigated. None of the twelve substituted acids gives mixed crystals with BzOH. Mixed crystals are formed by the similarly oriented chloro- and methyl-benzoic acids whereas the hydroxybenzoic acids do not form mixed crystals with the corresponding chloro- and methyl-benzoic acids. The three bromobenzoic acids give mixed crystals with the similar chloro- and methyl-benzoic acids but not with the OH-acids. Mixed crystals are never observed with combinations of position isomerides with the same substituents or, as far as observations have been made, with different substituents. Relationships in this series differ from those recorded for derivatives of C₁₀H₈. There is no known exception to the isomorphous replaceability of Cl and Br but with other substituents this ability can be very greatly influenced by the complete structure of the mol. H. W.

Coupling of diazonium salts with derivatives of cyclic β -ketonic acids. R. P. LINSTAD and A. B. L. WANG (J.C.S., 1937, 807—814).—Et cyclopentanone-2-carboxylate (I) condenses with diazotised NH₂Ph to the phenylhydrazone (cf. A., 1926, 1151) of Et H α -keto adipate, with some cyclopentane-1:2-dionemonophenylhydrazone, m.p. 201—203°, converted by NPh·NH₂ into the osazone. Using *o*- or *p*-NO₂·C₆H₄·NH₂, cyclopentane-1:2-dione-mono-*o*- (II) (dimorphous, yellow and orange), m.p. 176—177°, and -mono-*p*-nitrophenylhydrazone (III), m.p. 242°, are obtained. By action of aq. EtOH-KOH, (II) undergoes ring fission to ω -aldehydovaleic acid *o*-nitrophenylhydrazone, m.p. 170—172°. With the diazonium salt from 2:4-(NO₂)₂C₆H₃NH₂, (I) gives Et 2-(2':4'-dinitrobenzeneazo)cyclopentanone-2-carboxylate, m.p. 162—164°, which with aq. Na₂CO₃ undergoes

acid fission to *Et H* α -ketoadipate 2:4-dinitrophenylhydrazone, m.p. 168—170° (decomp.), hydrolysed to α -ketoadipic acid 2:4-dinitrophenylhydrazone, m.p. 238—240° (decomp.) (*Et*₂ ester, m.p. 48—50°). With NH₂Ph in C₅H₅N and xylene, (I) gives cyclopentanone-2-carboxyanilide (IV), with its *anil*, m.p. 128—129°; with NH₂Ph and a trace of AcOH, (I) yields *Et* 1-anilino- Δ^1 -cyclopentene-2-carboxylate, m.p. 58.5° (cf. A., 1929, 1312). Biscyclopentanone-2-carboxybenzidide (V), no m.p. <250°, is also prepared. With *o*- and *p*-NO₂·C₆H₄·N₂Cl, (IV) gives 2-*o*-, m.p. 177°, and 2-*p*-nitrobenzeneazocyclopentanone-2-carboxyanilide, m.p. 242°, with (II) and (III), respectively. 2-(2':4'-Dinitrobenzeneazo)cyclopentanone-2-carboxyanilide, m.p. 206—207°, and, from (V), bis-2-*o*-, m.p. 265—268° (decomp.), and bis-2-*p*-nitrobenzeneazocyclopentanone-2-carboxybenzidide, m.p. 245—250° (decomp.), are also prepared.

The product from *Et* cyclohexanone-2-carboxylate (VI) and NH₂Ph, *Et H* α -ketopimelate phenylhydrazone (A., 1931, 363), is hydrolysed by EtOH-KOH to α -ketopimelic acid phenylhydrazone, m.p. 153—154°, reduced to α -aminopimelic acid. *Et H* α -ketopimelate *p*-nitrophenylhydrazone (VII), m.p. 150°, and α -ketopimelic acid *p*-nitrophenylhydrazone, m.p. 174—175°, are also prepared. With *p*-nitrobenzenediazonium sulphate (VIII), (VI) yields *Et* 2-*p*-nitrobenzeneazocyclohexanone-2-carboxylate, m.p. 130—131°; this, which shows no tendency towards ring-fission, is converted by aq. Na₂CO₃ into (VII). Hydrolysed (VI), or pure cyclohexanone-2-carboxylic acid, with diazotised NH₂Ph or *p*-NO₂·C₆H₄·NH₂, gives cyclohexane-1:2-dione-phenylhydrazone (A., 1933, 835) and -mono-*p*-nitrophenylhydrazone, m.p. 245—246° (of which the phenylhydrazone, m.p. 243—244°, is prepared, in orange and blue dimorphic forms); the last is also the product when (VIII) is used, no azo-acid being formed. With cyclohexanone-2-carboxyanilide, (VIII) gives 2-*p*-nitrobenzeneazocyclohexanone-2-carboxyanilide, m.p. 214°. 1-Phenyl-3:4-cyclohexano-5-pyrazolone (IX) and (VIII) give a crude azopyrazolone, which with boiling EtOH yields (IX), MeCHO, PhNO₂, and N₂, and with NPhMe₂ gives *p*-nitrobenzeneazodimethylaniline.

E. W. W.

Derivatives of salicylic acid. XI. Bromosalicylic acids and their methyl ethers. N. W. HIRWE and B. V. PATIL. XII. N. W. HIRWE and (Miss) K. D. GAVANKER (Proc. Indian Acad. Sci., 1937, 5, A, 321—325, 377—380).—XI. 3-Bromo- is prepared from 5-sulpho-salicylic acid by brominating and passing steam through its conc. aq. solution at 130°, and its *Me* ester, b.p. 277—278°, from the Ag salt and MeI. Other new derivatives described are those of 3-bromo- (*Et* ester, b.p. 270°; *amide*, m.p. 105—106°), 5-bromo- (*Et* ester, b.p. 295°; *amide*, m.p. 153—154°), and 3:5-dibromo- (*Et* ester, b.p. 295°; *amide*, m.p. 173—174°) -2-methoxybenzoic acid.

XII. The following are described: *Me* 3-, m.p. 60°, and *Et* 5-nitro-2-methoxybenzoate, m.p. 80—81°; 3-, m.p. 124°, and 5-nitro-, m.p. 213°, and 3:5-dinitro-2-methoxybenzamide, m.p. 166—167°; 3-nitro-5-bromo-, m.p. 221°, and 3:5-dinitro-, m.p. 181°, -2-hydroxybenzamide.

A. Li.

Preparation of *o*-phthalaldehydic acid. B. B. DEY and T. K. SRINIVASAN (Proc. Indian Acad. Sci., 1937, 5, A, 329—335).—C₁₀H₈ is oxidised (KMnO₄) to phthalonic acid, the NaHSO₃ derivative of which (cf. Graebe and Trümpy, A., 1898, i, 318), after two evaporations with conc. HCl, yields dipthalide ether (I) (hydrolysed by NaOH to *o*-CHO·C₆H₄·CO₂H) and a compound (extracted with C₆H₆), C₁₆H₁₂O₆, m.p. 98°, clearing point 168°, probably C₆H₄<CH(OH)-O-CO-CO-O-C₆H₄(OH)>C₆H₄ (II), which gives with boiling H₂O or conc. HCl *o*-CHO·C₆H₄·CO₂H, and with boiling EtOH (I) and ψ -phthalaldehydic *Et* ester. Applying these observations, the yield of phthalaldehydic acid from the phthalonic acid by the method of Gardener and Naylor (Org. Syntheses, 1936, 16, 68) can be made as high as 77% by working up the residue left after the C₆H₆ extraction. The NO₂-derivative of (II) (KNO₃ + H₂SO₄), m.p. 120—140°, is hydrolysed to 1:2:3-NO₂·C₆H₄(CHO)·CO₂H.

A. Li.

Condensation of aldehydes with malonic acid in presence of organic bases. VIII. Condensation of *o*- and *m*-anisaldehyde. K. C. PANDYA and T. A. VAHIDY (Proc. Indian Acad. Sci., 1937, 5, A, 437—441; cf. A., 1936, 1377).—The yields of *o*- (or *m*-)methoxycinnamic acid afforded by condensing of *o*- (or *m*-)anisaldehyde with CH₂(CO₂H)₂ in presence of five different bases are compared. C₅H₅N gives the best yield (100%) and cleanest product, but condensation also occurs (more slowly) without using a base.

F. N. W.

Friedel-Crafts condensation of substituted glutaric anhydrides with benzene and the formation of isomeric benzoylphenylpropionic acids in the reaction between phenylsuccinic anhydride and benzene. A. ALI, R. D. DESAI, R. F. HUNTER, and S. M. M. MUHAMMAD (J.C.S., 1937, 1013—1016).—The anhydrides of glutaric acid and its β -Me₂ and β -methyl- β -ethyl derivatives react with C₆H₆ (AlCl₃) to give γ -benzoyl-*n*-butyric acid, m.p. 132° [semicarbazone, m.p. 213° (decomp.)], β - β -dimethyl-*n*-butyric acid, b.p. 115°/35 mm. [semicarbazone, m.p. 178° (decomp.)], and β -methyl- β -ethyl-*n*-butyric acid, m.p. 49° [semicarbazone, m.p. 164—165° (decomp.)]. These are reduced (Clemmensen) to CH₂Ph·[CH₂]₃·CO₂H, δ -phenyl- β - β -dimethyl-, b.p. 120—121°/15 mm., and δ -phenyl- β -methyl- β -ethyl-*n*-valeric acid, b.p. 138°/20 mm., but with H₂SO₄ none of these condenses to the expected benzocycloheptane derivative, there being extensive sulphonation. β -Phenylglutaric anhydride does not condense with C₆H₆, but internally, giving ketohydrindene-3-acetic acid [semicarbazone, new m.p. 260° (decomp.)]. CPh·CHBz and CHNa(CO₂Et)₂ give a substance, m.p. 255°, and CH₂Bz·CHPh·CH₂·CO₂H. cyclopentane-1:1-di-acetic anhydride with C₆H₆ and AlCl₃ gives 1-phenacylcyclopentane-1-acetic acid, m.p. 85° [semicarbazone, m.p. 196° (decomp.)], reduced to 1- β -phenylethylcyclopentane-1-acetic acid, an oil, with 1- β -hydroxy- β -phenylethylcyclopentane-1-acetic acid lactone (?), m.p. 216°. 1-Phenacyl-3-methylcyclopentane-1-acetic acid, m.p. 65° [semicarbazone, m.p. 187° (decomp.)], is prepared. 1-Phenacylcyclohexane-1-acetic acid, m.p.

99° [semicarbazone, m.p. 189° (decomp.)], is reduced to 1- β -phenylethylcyclohexane-1-acetic acid, an oil, with 1- β -hydroxy- β -phenylethylcyclohexane-1-acetic acid lactone (?), m.p. 265°. In the condensation of phenylsuccinic anhydride with C_6H_6 ($AlCl_3$), in addition to β -benzoyl- β -phenylpropionic acid (I) (reduced to β -diphenylbutyric acid), β -benzoyl- α -phenylpropionic acid (II), m.p. 154° (reduced to α -diphenyl-n-butyric acid, m.p. 110°), and γ -hydroxy- α - γ [or β]-triphenyl-n-butyric acid lactone (?), m.p. 285° (decomp.), are formed. The compounds (I) and (II) are synthesised from CH_2PhBz , $NaOEt$, and $CH_2Br \cdot CO_2Et$ and from $CH_2Ph \cdot CN$ and CH_2BzBr , respectively.

E. W. W.

Bridged ring systems. Density, refraction, and hydrolysis of esters. H. BODE (Ber., 1937, 70, [B], 1167—1186).—Measurements of d and n are recorded for the isomeric Me_2 3:6-*endo*methylenehexahydrobenzoates, Me_2 3:6-*endo*methylenehexahydro-*o*-phthalates, and Me_2 3:6-*endo*methylene- Δ^4 -tetrahydro-*o*-phthalates. The *endo*- and *endo-cis*-forms are the most compact; the *exo*- and *exo-cis*-isomerides have somewhat greater mol. vols. whilst the *trans*-isomerides have the largest vols. The differing mol. vols. are probably caused by difference in size of the individual mols. rather than by differences in the intermol. forces. The mol. refraction of isomeric esters is practically const. The abs. vals. of the mol. refraction agree well with those calc. according to Roth-Eisenlohr particularly in the cases of the saturated esters. This is attributed to compensation of the diminution of polarisability caused by the compact, spatial structure of the mol. by the strain in the mol. In a corresponding strainless mol. (Me_2 *cis*-3:6-*endo*ethylene- Δ^4 -tetrahydro-*o*-phthalate and the corresponding H_6 compound; dicyclohexadiene; tetrahydrodicyclohexadiene) a depression of the mol. refraction is observed. Examination of recorded rates of hydrolysis of esters of borneol and isoborneol and the corresponding *epi*-compounds shows that, for each corresponding pair, one form (*iso*-alcohols, α -esters) is characterised by higher d and n and smaller rate of hydrolysis and can be converted into the other isomeride. The mol. refractions of each isomeride are equal. In properties, therefore, the isomerides correspond completely with the *endo-exo*-compounds of the norcamphane series and, if the rules developed for the latter are applied, the isoborneol, *epi*-isoborneol, and α -acid derivatives are to be regarded as isomerides with *endo*-placed groups.

H. W.

Identification of alcohols by 3-nitrophthalic anhydride. G. M. DICKINSON, L. H. CROSSON, and J. E. COPENHAVER (J. Amer. Chem. Soc., 1937, 59, 1094—1095).—The following *alkyl H* 3-nitrophthalates, 3:1:2- $NO_2 \cdot C_6H_3(CO_2H) \cdot CO_2R$, are obtained, with a little of the 1-mono-ester, by heating the acid anhydride and alcohol at the b.p., at 100°, or in $PhMe$: Me , m.p. 152.9—153.4°, Et , m.p. 157.7—158.3°, Pr^a , m.p. 144.9—145.7°, Pr^b , m.p. 153.9—154.3°, Bu^a , m.p. 146.8—147°, Bu^b , m.p. 179.9—180.6°, *sec*- Bu , m.p. 130.6—131.4°, *n*-*amyl*, m.p. 136.2—136.4°, *isoamyl*, m.p. 163.2—163.4°, *n*-*hexyl*, m.p. 123.9—124.4°, *n*-*heptyl*, m.p. 126.9—127.2°, *n*-*octyl*,

m.p. 127.8—128.2°, *n*-*nonyl*, m.p. 124.8—125.2°, *n*-*decyl*, m.p. 122.7—122.8°, *n*-*undecyl*, m.p. 123.2—123.3°, *n*-*dodecyl*, m.p. 123.9—124°, *n*-*tridecyl*, m.p. 124—124.2°, *n*-*tetradecyl*, m.p. 123.2—123.5°, *n*-*pentadecyl*, m.p. 122.4—122.6°, *n*-*hexadecyl*, m.p. 121.4—122°, *n*-*heptadecyl*, m.p. 121—121.8°, and *n*-*octadecyl*, m.p. 118.3—119.2°. M.p. are corr. R. S. C.

Reaction between phthalic anhydride and ethylene glycol.—See A., I, 417.

Optical resolution of 1:1'-dianthryl-2:2'-dicarboxylic acid. K. LAUER, R. ODA, and M. MIYAWAKI (J. pr. Chem., 1937, [ii], 148, 310—316).—Fractional crystallisation of the quinine salt of the *dl*-acid affords quinine d-1:1'-dianthryl-2:2'-dicarboxylate (I), m.p. 165—185° (decomp.), $[\alpha]_D^{20} +233.2^\circ$ in $CHCl_3$, and quinine l-1:1'-dianthryl-2:2'-dicarboxylate (II), m.p. 160—185° (decomp.), $[\alpha]_D^{20} -245.0^\circ$ in $CHCl_3$. (I) and HCl afford d-1:1'-dianthryl-2:2'-dicarboxylic acid (III), m.p. 187—198° (decomp.), $[\alpha]_D^{20} +352.0^\circ$ in $COMe_2$ (chloride, $[\alpha]_D^{20} +256.0^\circ$ in $CHCl_3$; amide, m.p. 171—175°, $[\alpha]_D^{20} +250.0^\circ$ in $CHCl_3$). Similarly, (II) affords l-1:1'-dianthryl-2:2'-dicarboxylic acid (IV), m.p. 190—200° (decomp.), $[\alpha]_D^{20} -358.2^\circ$ in $COMe_2$ (chloride, $[\alpha]_D^{20} -250.0^\circ$ in $CHCl_3$; amide, m.p. 172—180°, $[\alpha]_D^{20} -251.5^\circ$ in $CHCl_3$), converted by $NaOBr$ into l-2:2'-diamino-1:1'-dianthryl, m.p. 174—175°, $[\alpha]_D^{20} -336.7^\circ$ in $CHCl_3$. (IV) was not racemised in Ac_2O solution at 145° for 5 hr. The esterification rates, and $[\alpha]_D^{20}$ vals. in $CHCl_3$, $AcOH$, and 0.1*N*- KOH , of (III) and (IV) are given, as well as X-ray (powder) figures for (III).

P. G. C.

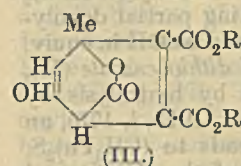
Diene synthesis. II. Thermal decomposition of the additive products of acetylenedicarboxylic ester. K. ALDER and H. F. RICKERT (Ber., 1937, 70, [B], 1354—1363).—*cyclo*Heptadiene (I) and $CO_2Me \cdot C \equiv C \cdot CO_2Me$ give the normal adduct, hydrogenated (colloidal Pd), hydrolysed, and dehydrated by $AcCl$ to 3:6-*endo*propylene- Δ^1 -tetrahydrophthalic anhydride, m.p. 137°. (I) therefore resembles *cyclopentadiene*. Furan is heated with $CO_2Et \cdot C \equiv C \cdot CO_2Et$ at 100° and the product is hydrogenated ($Pd-CaCO_3$) and then hydrolysed to 3:6-*endo-oxido*- Δ^1 -tetrahydrophthalic acid (II), m.p. 167°, and furan-

$H_2 \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \begin{array}{c} CO_2H \\ CO_2H \end{array}$ 3:4-dicarboxylic acid, m.p. 212° (Me ester, m.p. 46°). When treated similarly, 2-methylfuran yields 2-methylfuran-3:4-dicarboxylic acid, m.p. 230—231° (non-cryst. Me_2 ester; dianilide, m.p. 211—212°), and 3:6-*endo-oxido*-3-methyl- Δ^1 -tetrahydrophthalic acid, degraded to 3-methylphthalic acid, m.p. 154° (anhydride, m.p. 118°). When boiled with

$CO_2Et \cdot C \equiv C \cdot CO_2Et$. Et isodehydracetate gives CO_2 and (after hydrolysis) 5-carbethoxy-4:6-dimethyl-*o*-phthalic acid, m.p. 164° (K_2 salt), oxidised by fuming HNO_3 at 130—140° to $C_6H(CO_2H)_5$. Analogously, trimellitic acid is derived from Et cou-

malate. 4-Methylpyrone reacts as enol giving a primary adduct (III), which becomes stabilised by loss of CO_2 and formation of an aromatic nucleus whereby 5-hydroxy-*m*-toluic acid is obtained in place of the expected 4-hydroxy-6-methyl-*o*-phthalic acid.

H. W.



Synthesis of conjugated bile acids. III. Sodium taurocholate and taurodeoxycholate. F. CORTESE and J. T. BASHOUR (J. Biol. Chem., 1937, 119, 177—183; cf. A., 1936, 724).—The chloride of trimethylcholic acid (I) with conc. aq. taurine (II) and conc. aq. NaOH [amount required depending on purity of (I)] are shaken for 5 hr., and neutralised with HCl. COMe_2 is added, and recovered (II) removed. The filtrate is evaporated, and the boiling EtOH extract of the resulting oil or gum is pptd. with Et_2O , giving Na trimethyltaurocholate. This is treated with NaOH, followed by HCl, and Na taurocholate (III) obtained in 50% yield, $[\alpha]_D^{20} +23.7^\circ$ in H_2O , identical with the natural product. Decomp. points of normal (130—145°) and *para* (225—235°) forms of (III) are of little val. for characterisation. The amount of H_2O in (III) depends on atm. R.H. The chloride from diformyldeoxycholic acid (*loc. cit.*) with taurine similarly gives Na taurodeoxycholate (IV), $[\alpha]_D^{20} +35.4^\circ$, which at 117° gives a *para* form, decomp. 160—175°. Full details of prep. of (III) and (IV) are given. The work of Tanaka (A., 1933, 1162) is criticised: (III) does not isomerise in H_2O at 100°. The Bondi and Müller method (cf. A., 1919, i, 576) yields (IV) and not the free acid.

E. W. W.

Sulphur studies. XI. Sulphur derivatives of benzaldehyde. J. H. WOOD and R. W. BOST (J. Amer. Chem. Soc., 1937, 59, 1011—1013).—When CHPhCl_2 and Na_2S are kept in EtOH under N_2 for a week or heated for 6—8 hr., PhCHS is formed, but cannot be isolated; some gives the β -trimeride (I), some undergoes the Cannizzaro reaction to give $\text{CH}_2\text{Ph}\cdot\text{SH}$, PhCS_2H , and a little $\text{PhCS}_2\cdot\text{CH}_2\text{Ph}$ (II), whilst some of the $\text{CH}_2\text{Ph}\cdot\text{SH}$ formed reacts with PhCHS to give a little $\text{CHPh}(\text{S}\cdot\text{CH}_2\text{Ph})_2$. PhCHS undergoes the Cannizzaro reaction by way of the ester (II); if it is brought about by Na_2S , the ester cannot be isolated owing to its immediate hydrolysis to PhCS_2H and $\text{CH}_2\text{Ph}\cdot\text{SH}$, but if (I) is distilled at 3 mm. in the presence of a few drops of H_2SO_4 , the distillate is mainly the monomeride [with a little $(\text{CHPh})_2$, S, and tetraphenylthiophen], which partly reverts to (I) and partly polymerises to (II); the Cannizzaro reaction can then be completed by adding Na_2S . When (I) is distilled alone, tetraphenylthiophen is the main product. Passage of H_2S into PhCHO in EtOH saturated with HCl gives (I); in presence of less acid [HCl , H_2SO_4 , ZnCl_2 , AcOH , $\text{Mg}(\text{ClO}_4)_2$, P_2O_5], a pink gummy polymeride is formed, which decomposes when distilled, mainly into $(\text{CHPh})_2$ and S, and does not undergo the Cannizzaro reaction. Passage of H_2S into PhCHO in KOH-EtOH gives mainly a pink oily polymeride, and a residue, which undergoes the Cannizzaro reaction; distillation of this polymeride gives mainly $(\text{CHPh})_2$ and S, but also some (II), indicating partial depolymerisation. PhCS_2Na , CH_2PhCl , and NaOH in equiv. amounts in hot EtOH give *benzyl dithiobenzoate* (II), b.p. 179—180°/3 mm., identified by hydrolysis by Na_2S ; contrary to Fromm *et al.* (A., 1913, i, 175), an excess of CH_2PhCl and NaOH leads to $(\text{CH}_2\text{Ph})_2\text{S}$, m.p. 50°, obtained by hydrolysis of the (II) formed and interaction of the resulting $\text{CH}_2\text{Ph}\cdot\text{SNa}$ with CH_2PhCl . $(\text{CHPh}\cdot\text{NH}\cdot\text{HCl})_2$, SnCl_4 and H_2S in EtOH

give a plastic substance, m.p. 100—110°, and a pink gum.
R. S. C.

κ -Phenylundecapentaenal and ϕ -phenylpenta-decaheptaenal. R. KUHN and K. WALLENFELS (Ber., 1937, 70, [B], 1331—1333).— $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ is transformed by $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ in presence of piperidine-AcOH into κ -phenylundecapentaenal (I), m.p. 183° (vac.), the constitution of which is established by its conversion by $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ into $\text{Ph}\cdot[\text{CH}\cdot\text{CH}]_6\cdot\text{Ph}$. Condensation of (I) with $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ containing piperidine affords *phenylundecapentaenylidenemalonic acid*, decarboxylated in boiling Ac_2O to μ -phenyl- $\Delta^{\alpha,\gamma,\epsilon,\delta}$ -tridecahexaenoic acid, m.p. 255°. (I) is reduced by $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH to λ -phenyl- $\Delta^{8,10,\kappa}$ -undecapentaenol, m.p. 203°. ϕ -Phenylpenta-decaheptaenal, m.p. 234°, is obtained in minor amount during the prep. of (I).
H. W.

Studies in the synthesis of vitamin-A. III. J. W. BATTY, A. BURAWOY, I. M. HELLBRON, W. E. JONES, and A. LOWE (J.C.S., 1937, 755—760).—Experiments directed towards the synthesis of ϵ -(2:2:6-trimethyl- Δ^6 -cyclohexenyl)- $\Delta^{8,10,\kappa}$ -nonatetraen- α -ol by way of ϵ -(2:2:6-trimethyl- Δ^6 -cyclohexenyl)acetaldehyde are described. The view (A., 1931, 961) that "citrylidenemalonic acid" is not δ -dimethyl- $\Delta^{\alpha,\gamma}$ -nonatriene- $\alpha\alpha$ -dicarboxylic acid is confirmed by its lack of selective absorption, and its failure to give COMe_2 when treated with O_3 . Its quant. conversion by Cu-bronze at 130—140°/10—15 mm. into δ -dimethyl- $\Delta^{\alpha,\gamma}$ -nonatriene- α -carboxylic acid (I), b.p. 132—134°/1 mm. (*Me* ester, b.p. 137—140°/15 mm.), is, however, difficult to reconcile with the dilactonic formula (*loc. cit.*). The Ba salt of (I) with $(\text{HCO}_2)_2\text{Ba}$ and sand at 150—160°/1 mm. gives α -aldehyde- δ -dimethyl- $\Delta^{\alpha,\gamma}$ -nonatriene (II) (citrylideneacetaldehyde; cf. A., 1936, 316), which with aq. $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ yields α -cyano- ζ -dimethyl- $\Delta^{\alpha,\gamma,\epsilon}$ -undecatetraene- α -carboxylic acid, m.p. 150°. (II) forms only one semicarbazone, m.p. 167° (cf. *loc. cit.*), but this is accompanied by a small quantity of a semicarbazone (III), m.p. 158° (see below). Citral condenses with $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ ($\text{C}_5\text{H}_{11}\text{N}\cdot\text{AcOH}$) at 110° (CO_2) to a product separated into three fractions. Fraction A is an oil, b.p. 86—88°/0.03 mm. [semicarbazone, $\text{C}_{15}\text{H}_{23}\text{ON}_3$ (IV), m.p. 206°; phenylhydrazone, $\text{C}_{21}\text{H}_{27}\text{ON}_3$, m.p. 173°]. Fraction B, b.p. 115—118°/0.1 mm., gives (IV) and (III) (see above), m.p. 160°, identified as the semicarbazone of α -aldehyde- ζ -dimethyl- $\Delta^{\alpha,\gamma,\epsilon}$ -undecatetraene (V), b.p. 114—118°/0.05 mm. (phenylsemicarbazone, m.p. 134°; 2:4-dinitrophenylhydrazone, m.p. 104—105°; anil, b.p. 178—182°/15 mm.), into which it is converted by $\text{H}_2\text{C}_2\text{O}_4$. With O_3 , (V) gives COMe_2 and lävul-aldehyde. Fraction C yields a semicarbazone, $\text{C}_{15}\text{H}_{23}\text{ON}_3$, m.p. 197°. Microhydrogenation of (III) shows 5 double linkings. λ_{max} and ϵ_{max} of the above compounds are tabulated.
E. W. W.

Polymethylbenzenes. XVII. Acetopentamethylbenzene. L. I. SMITH, (MISS) I. M. WEBSTER, and C. GUSS (J. Amer. Chem. Soc., 1937, 59, 1078—1082).—Acetopentamethylbenzene (I), prepared by Smith and Guss' method (this vol., 293), has b.p. 144—145°/8 mm., m.p. 84°, is completely enolised by MgEtBr , and the enolic OMgBr -compound with AcCl gives pentamethylbenzoyldiacetylmethane [γ -penta-

methylbenzoylpentane- $\beta\delta$ -dione] (II), m.p. 110—111° (Cu derivative), which with NH_2OH gives a compound, m.p. 176°, 4-pentamethylbenzoyl-3:5-dimethyl- or 4-acetyl-5-pentamethylphenyl-3-methyl-isooxazole. $\text{C}_6\text{Me}_5\text{MgBr}$ with AcCl by most procedures gives mainly C_6HMe_5 with some $\text{C}_6\text{Me}_5\text{Br}$ and (?) CMeEt_2OH ; methods of separating (I) and (II) from such reaction products are devised, but only in one case was (I) (6% only) found. Clémont's compound, m.p. 110° (A., 1936, 852), was not (I) or (II).

[With J. H. PADEN.] C_6HMe_5 , $\text{Zn}(\text{CN})_2$, HCl , and AlCl_3 give pentamethylbenzaldehyde, m.p. 142—147°, b.p. 144°/6 mm. (oxime, m.p. 187—188°; semicarbazone, m.p. 270—275°) (cf. Clémont, *loc. cit.*).

R. S. C.

Benzoyl chloride. Aromatic ketones. J. B. SENDERENS (Compt. rend., 1937, 204, 1296—1299).—When a mixture of BzCl and a fatty acid is passed over ThO_2 at 400—450°, the product contains the mixed fatty-aromatic ketone and the fatty ketone, with decomp. products of BzCl . Thus $\text{Pr}^n\text{CO}_2\text{H}$ gives COPhPr^n and COPr^n_2 at 450°; AcOH at 300° gives only COMe_2 whilst COPhMe appears at 400°. BzCl alone over ThO_2 at 370° decomposes to a gas (60% H_2 , 40% CO_2), HCl , H_2O , and C. A mixture of BzCl and glacial AcOH in a closed flask at room temp. slowly deposits crystals and evolves HCl ; the crystals when distilled give AcOH and BzOH . AcOH from Ac_2O does not react thus but propionic, butyric, and valeric acids (commercial pure) give small amounts of BzOH .

J. L. D.

Hydrolysis of esters, and the Knoevenagel reaction.—See A., I, 417.

Condensation of deoxybenzoin with aromatic aldehydes and ketones. II. Condensations using substituted deoxybenzoins and substituted acetophenones. H. J. CALLOW and D. W. HILL (J.C.S., 1937, 844—847; cf. A., 1936, 997).— COPhMe and deoxybenzoin in EtOH-KOH , exposed to air, give phenacylidenedideoxybenzoin, $\text{CHBz}(\text{CHPhBz})_2$ (I), m.p. 199—200°, and isophenacylidenedideoxybenzoin, m.p. 175°. These are shown to be stereoisomerides by their being both dehydrated by AcOH-HCl or by H_2SO_4 to the same substance, m.p. 118—119°, which is either 4-benzoyl-2:3:5-tetraphenylpyran or 4- α -phenylphenacyl-2:3:5-triphenylfuran. It is suggested that the above reaction proceeds through an intermediate oxide,

$\text{OH}\cdot\text{CPh}\begin{smallmatrix} \text{O}\cdot\text{CHPh} \\ \text{CHPh}\cdot\text{O} \end{smallmatrix}\text{CPh}\cdot\text{OH}$, which either reacts with COPhMe to form (I), or oxidises further to $\text{CHPh}\cdot\text{CPh}\cdot\text{OH}$, and thence to BzOH , which is also

obtained. Substituted deoxybenzoins give similarly phenacylidene-di-(4-methyldeoxybenzoin), m.p. 238—240° (and the iso-compound, m.p. 175—176°); -di-(4'-methyldeoxybenzoin), m.p. 255—256° (and the iso-compound, m.p. 240—241°); -di-(4-methoxydeoxybenzoin), m.p. 225° (and the iso-compound, m.p. 190°); -di-(4-chlorodeoxybenzoin), m.p. 255—256° (and the iso-compound, m.p. 211—212°); -di-(4'-chlorodeoxybenzoin), m.p. 248° (and the iso-compound, m.p. 234—235°), and -di-(4-bromodeoxybenzoin), m.p. 248° (from 4-bromodeoxybenzoin, m.p. 115°, prepared from p-

bromobenzamide and CH_2PhMgBr). With the above compounds, the corresponding benzoic acid is also formed. Using deoxybenzoin and substituted acetophenones, p-methyl-, m.p. 217° (iso-compound, m.p. 196—197°), p-methoxy-, m.p. 209° (iso-compound, m.p. 190—191°), p-bromo-, m.p. 231° (iso-compound, m.p. 213—215°), and p-amino-phenacylidenedideoxybenzoin, m.p. 205°, are obtained. E. W. W.

Reactions of α -aminoketones. T. S. STEVENS and B. A. HEMS (J.C.S., 1937, 856—857).—That N in compounds of type $\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{NMe}_2)\cdot\text{CH}_2\text{Ph}$ (I) (cf. A., 1930, 1437) occupies the α - and not the β -position with respect to CO , is shown by conversion of (I) by MgPhBr into β -dimethylamino- α -hydroxy- $\alpha\gamma$ -triphenylpropane, m.p. 75° (picrate, m.p. 188°), which is oxidised by persulphate to COPh_2 and $\text{CH}_2\text{Ph}\cdot\text{CHO}$. Substituted benzylacetophenones (*loc. cit.*) similarly give β -dimethylamino- α -hydroxy- $\alpha\gamma$ -triphenylbutane, not cryst. [hydrochloride, m.p. 226—231° (decomp.)], oxidised to COPh_2 and $\text{CHPhMe}\cdot\text{CHO}$; β -piperidino- α -hydroxy- $\alpha\gamma$ -triphenylpropane, m.p. 145—147°; and β -dimethylamino- α -hydroxy- $\alpha\gamma\gamma$ -tetraphenylpropane, m.p. 105° (sulphate), oxidised to COPh_2 , without $\text{CHPh}_2\cdot\text{CHO}$ or $\text{CHPh}_2\cdot\text{CO}_2\text{H}$. In EtOH-NaOEt , (I) is oxidised by air to Ph α -dimethylaminostyryl ketone, m.p. 62° (synthesised), with BzOH and $\text{CH}_2\text{Ph}\cdot\text{CPh}(\text{OH})\cdot\text{CO}_2\text{H}$. BrCN in Et_2O converts (I), with loss of a Me group, into Ph α -methylcyanoamido- β -phenylethyl ketone, m.p. 110° (corresponding carbamide, m.p. 226°). ω -Piperidino- ω -benzylacetophenone similarly gives, by ring fission, Ph α -(ϵ -bromoamylcyanoamido)- β -phenylethyl ketone, m.p. 83°. E. W. W.

Detection and determination of aldehydes by halogen derivatives of dimedon. T. VOITILA (Suomen Kem., 1937, 10, B, 14).—Reduction of 2:4:6-tribromo-1:1-dimethylcyclohexane-3:5-dione with acid KI yields 2:6-dibromo-1:1-dimethylcyclohexane-3:5-dione (I), m.p. 145—147° (decomp.). (I) (2 mols.) gives with CH_2O (1 mol.) a compound, m.p. 203—204°, and with MeCHO (1 mol.) a compound, m.p. 182° (decomp.). 4-Bromo-1:1-dimethylcyclohexane-3:5-dione reacts with CH_2O with loss of HBr , the product having m.p. 213—214°. M. H. M. A.

Pyrenium. XXVIII. Constitution of benzoylnaphthol. W. DILTHEY and O. DORNHEIM (J. pr. Chem., 1937, [ii], 149, 55—57).—The action of MgPhBr on 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{CHO}$ gives phenyl-2-hydroxy-1-naphthylcarbinol, m.p. 118—119°, also obtained by reduction of 1:2- $\text{C}_{10}\text{H}_7\text{Bz}\cdot\text{OH}$ (I) in alkaline but not in acid medium. The constitution of (I) is thus established. H. W.

Synthesis of dicyclic α -ketones with an angular methyl group. G. A. R. KON, R. P. LINSTAD, and C. SIMONS (J.C.S., 1937, 814—817).—8-Methyl-1-hydrindanone and 9-methyldecahydronaphthal-1-one are synthesised by new methods. With $\text{OEt}\cdot[\text{CH}_2]_3\cdot\text{MgBr}$, Et 2-methylcyclohexanone-2-carboxylate gives Et 2-methyl-2- γ -ethoxypropylcyclohexan-1-ol-2-carboxylate (cf. this vol., 197), b.p. 144°/4 mm., which when boiled with aq. $\text{H}_2\text{C}_2\text{O}_4$ gives Et 2-methyl-1- γ -ethoxypropyl- Δ^{6m} -cyclohexene-2-carboxylate, b.p. 122°/2 mm., reduced (Adams) to

Et 2-methyl-1- γ -ethoxypropyl- $\Delta^{6(1)}$ -cyclohexane-2-carboxylate (I), b.p. 123°/3 mm. (hydrolysed with difficulty to the acid). This with HI gives the *I*-acid (II), oxidised by CrO_3 -AcOH to 2-methylcyclohexane-2-carboxylic-1- β -propionic acid (III), also obtained from (I) by oxidation through the *OEt*-acid. When distilled with $\text{Ba}(\text{OH})_2$, (III) gives 8-methyl-1-hydrindanone, m.p. 33–34°, b.p. 84°/5 mm. (cf. A., 1936, 988) (semicarbazone, new m.p. 224·5°), which with conc. HNO_3 forms 2-methylcyclohexane-1-carboxylic-2-acetic acid. $\text{OEt} \cdot [\text{CH}_2]_3 \cdot \text{OH}$ gives rise to δ -ethoxybutyl bromide, b.p. 169°, which similarly furnishes *Et* 2-methyl-1- δ -ethoxybutylcyclohexan-1-ol-2-carboxylate, b.p. 165°/0·5 mm., *Et* 2-methyl-1- δ -ethoxybutyl- $\Delta^{6(1)}$ -cyclohexene-2-carboxylate, b.p. 135°/0·4 mm., and *Et* 2-methyl-1- δ -ethoxybutylcyclohexane-2-carboxylate, b.p. 149°/0·8 mm., hydrolysed to the acid. The *OEt*-acid with CrO_3 -AcOH, followed by $\text{Ba}(\text{OH})_2$ distillation, gives 9-methyldecahydronaphthal-1-one (cf. A., 1936, 988), also obtained by converting (II) by $\text{EtOH}-\text{H}_2\text{SO}_4$ into *Et* 2-methyl-1- γ -iodopropylcyclohexane-2-carboxylate, and treating this with KCN-EtOH. E. W. W.

Sterol group. XXXII. Bromination of 6-ketocholestanyl acetate. I. M. HEILBRON, E. R. H. JONES, and F. S. SPRING (J.C.S., 1937, 801–805).—Experiments directed towards the prep. of 7-dehydrocholesterol are described. 6-Ketocholestanyl acetate (I), with Br-AcOH at 0°, gives a 5-Br-derivative (II), m.p. 162° (decomp.), $[\alpha]_D^{25} -133^\circ$ (all rotations in CHCl_3). At the b.p. the product is the 7-Br-derivative (III), m.p. 144–145° (stable), $[\alpha]_D^{25} +41^\circ$. With HBr-AcOH, at 100°, (II) yields (III); both are reduced by Al-Hg to (I). In $\text{C}_5\text{H}_5\text{N}$, (II) gives 6-keto-3-acetoxy- Δ^4 -cholestene (IV), m.p. 110°, $[\alpha]_D^{25} -50\cdot5^\circ$, absorption max. at 2360 and 3200 Å., which is converted by MeOH-KOH at the b.p. into 3:6-diketocholestane (V), or, at room temp., into 3-hydroxy-6-keto- Δ^4 -cholestene, m.p. 150–151°, $[\alpha]_D^{25} -13^\circ$, absorption max. at 2390 and 3190 Å., which with hot EtOH-KOH yields (V). With $\text{Al}_2(\text{OPr}^i)_3$ - Pr^iOH , followed by MeOH-KOH, (IV) gives 3:6-dihydroxy- Δ^4 -cholestene, m.p. 178–179° [*Ac*, derivative, m.p. 154–155–157° (third temp. clearing point), $[\alpha]_D^{25} +24\cdot8^\circ$; *Bz*, derivative, m.p. 198–199–208°, $[\alpha]_D^{25} +83\cdot9^\circ$]. With EtOH-KOH, (II) gives 3:5-dihydroxy-6-ketocholestane, m.p. 138°, $[\alpha]_D^{25} +29\cdot3^\circ$ (*Bz* derivative, m.p. 170°, $[\alpha]_D^{25} +23\cdot0^\circ$). Conversion of (III) into (IV) was not effected, but on prolonged heating of (III) with AgNO_3 in $\text{C}_5\text{H}_5\text{N}$, 6:7-diketocholestanyl acetate, m.p. 156–157°, $[\alpha]_D^{25} -108^\circ$ (quinoxaline derivative, m.p. 186–187°), was obtained, and with EtOH-KOH, 3:7-dihydroxy-6-ketocholestane, m.p. 179°, sublimes at 220°/0·001 mm., $[\alpha]_D^{25} +31\cdot4^\circ$ (*Bz*, derivative, m.p. 169–170°, $[\alpha]_D^{25} +62\cdot0^\circ$). E. W. W.

Replacement of the 3-hydroxyl in pregnenolone and androstendiol by chlorine. A. BUTENANDT and W. GROSSE (Ber., 1937, 70, [B], 1446–1450).— Δ^5 -Pregnen-3-ol-20-one is converted by $\text{C}_6\text{H}_5\text{MeSO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ at room temp. into the *p*-toluenesulphonate, m.p. 139–140°, $[\alpha]_D^{25} +9^\circ$ in CHCl_3 , converted by MeOH at 100° into pregnenolone *Me ether*, m.p. 123–124°, $[\alpha]_D^{25} +18^\circ$ in CHCl_3 , and by

KOAc in boiling MeOH into isopregnenolone *Me ether*, m.p. 124–125°, $[\alpha]_D^{25} +132^\circ$ in CHCl_3 ; this with conc. HCl-AcOH at room temp. yields 3-chloro- Δ^5 -pregnen-20-one, m.p. 146·5°, $[\alpha]_D^{25} +31\cdot5^\circ$ in CHCl_3 (oxime, m.p. 181°). Androstene-3:17-diol di-*p*-toluenesulphonate, m.p. 140–141°, $[\alpha]_D^{25} -59^\circ$ in CHCl_3 , gives isoandrostenediol *Me ether* 17-*p*-toluenesulphonate, m.p. 124°, $[\alpha]_D^{25} +23\cdot5^\circ$ in CHCl_3 , whence 3-chloro- Δ^5 -androstene 17-*p*-toluenesulphonate, m.p. 150°, $[\alpha]_D^{25} -60^\circ$ in CHCl_3 . H. W.

Manufacture of 17-hydroxy-3-keto-compounds of the cyclopentanopolyhydrophenanthrene series.—See B., 1937, 620.

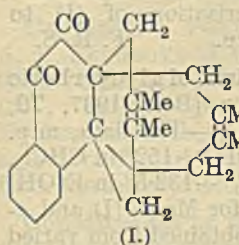
Constitution of shikonin. Syntheses of isohexylnaphthapurpurin and related compounds. (Miss) C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1937, 13, 158–160).—In a similar manner to the prep. of naphthapurpurin from naphthazarin (A., 1927, 886), isohexylnaphthazarin (this vol., 66) gives isohexylnaphthapurpurin [3:5:8-trihydroxy-2-isohexylnaphthaquinone] (I), m.p. 117°. 3:5:8-Trihydroxy-2-ethylnaphthaquinone, m.p. 195°, is obtained similarly, as is the 2-Me derivative [which on keeping changes its m.p. from 192° to 176° (subliming)]; the identity of the last with the known compound (A., 1935, 623) establishes the structure of (I). No details or analyses are given. E. W. W.

Salts of 1-aminoanthraquinone-2-carboxylic acid. J. V. DUBSKÝ, M. HRDLÍČKA, and K. ŠTĚPÁN (Publ. Fac. Sci. Univ. Masaryk, 1937, No, 232, 1–9).—Normal salts of Pb^{2+} , Hg^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , Ba^{2+} , Sr^{2+} , and Mg^{2+} are pptd. by adding equiv. amounts of these cations in solution to a carefully neutralised solution of the K salt (I) of the acid. A slightly alkaline solution of (I) gives the basic salts of Pb^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , and Ca^{2+} . All these salts are dark red in colour. Only the alkali and NH_4 salts are H_2O -sol. F. R.

Addition of dienes to halogenated and hydroxylated naphthaquinones. L. F. FIESER and J. T. DUNN (J. Amer. Chem. Soc., 1937, 59, 1016–1021).—Hydroxy-1:2-naphthaquinones decompose rather than add dienes, and OH-substituents depress the rate of reaction of the 1:4-quinone; 3- and 4-halogeno-1:2-naphthaquinones, however, condense readily with dienes to give adducts which readily lose HCl to alkali and then oxidise in air to phenanthraquinones. Prep. of the following is described: 6- and 7-hydroxy-1:2-naphthaquinone [do not condense with $(\text{CH}_2\text{CMe})_2$], juglone and its Ac derivative, m.p. 153–154°, 1:2:4:5- (or 1:2:4:8-)tetra-acetoxynaphthalene, m.p. 154°, 2:5- (or 2:8-) $\text{C}_{10}\text{H}_6(\text{OH})_2$, decomp. about 220°, naphthazarin diacetate, m.p. 195–196°, 5:6:8-triacetoxy-1:4-naphthaquinone, m.p. 165–166°, 3-bromo- (I), m.p. 177–178°, 3:4-dichloro- (II), m.p. 183·5–184·5°, and 4-chloro-1:2-naphthaquinone (III) (from 1:1-dichloro-2-ketodihydronaphthalene by way of 1:4-dichloro-2-naphthol and -1-nitro-2-ketodihydronaphthalene), m.p. 132–136° (decomp.). 6-Bromo-1:2-naphthaquinone and $(\text{CH}_2\text{CMe})_2$ give a product, oxidised during

reaction to a substance, $C_{16}H_{13}OBr$, m.p. 237—238° (decomp.). $(CH_2.CMe)_2$ forms adducts with acetyljuglone (94% in 30 min.), m.p. 126—128°, juglone (I) (95% in 20 min.), m.p. 141—142° [with $Ac_2O-NaOAc$ gives 5:9:10-triacetoxy-2:3-dimethyl-1:4-dihydroanthracene, m.p. 197—198°, converted by 10% KOH into 5-hydroxy-2:3-dimethylantraquinone, m.p. 178.5—179.5°, also obtained similarly from (I)], naphthazarin (83% in 6 hr.), m.p. 195° (decomp.), diacetylnaphthazarin (92% in 3 hr.), m.p. 175° (decomp.), 5:6:8-trihydroxy- (33% in 60 hr.), m.p. 255° (decomp.), and 5:6:8-triacetoxy- (70% in 27 hr.), m.p. 186° (decomp.), and 2-methyl-8-hydroxy-1:4-dihydroanthracene (84% in 19 hr.), m.p. 78—79.5° (decomp.). Juglone and $(CH_2.CH)_2$ give an adduct (94% in 30 min.), m.p. 124—125°. 3-Chloro-1:2-naphthaquinone in pure $CHCl_3$ affords with $(CH_2.CMe)_2$ an adduct, m.p. 87—88°, which rapidly decomposes when kept or when warmed with $NaOAc-EtOH$, yielding 2:3-dimethylphenanthraquinone, m.p. 237—238°, 242—243° (corr.), also obtained from (III) by way of an impure Cl-compound and from (I) by way of a Br-compound which was oxidised by CrO_3 . (II) gives an adduct with $(CH_2.CMe)_2$, m.p. 130.5—131.5°, which only slowly gives up Cl to hot 10% KOH-EtOH, yielding thereby an oil. R. S. C.

Further reaction product from 3-chloro-1:2-naphthaquinone and dimethylbutadiene. L. F. FIESER and J. T. DUNN (J. Amer. Chem. Soc., 1937, 59, 1021—1024).—When 3-chloro-1:2-naphthaquinone and $(CH_2.CMe)_2$ are heated at 100° in $CHCl_3$, the initial red colour fades to yellow in about 45 min. owing to addition to form 11-chloro-2:3-dimethyl-1:4:11:12-tetrahydrophenanthraquinone; in 35—50 min., particularly in light, the red colour returns, probably due to loss of HCl and formation of 2:3-dimethyl-1:4-dihydrophenanthraquinone; in a further 2 hr. the colour has faded again to yellow (green fluorescence) and the solution yields a substance, $C_{22}H_{24}O_2$, colourless and yellow forms, m.p. 135° after sintering at 130°, believed to be (I). (I) absorbs 2 O_2 from BzO_2H and with H_2O_2 gives 4:5-dimethyl-2:2'-diphenic acid, m.p. 203—204°, also obtained from 2:3-dimethylphenanthraquinone (II); it resists hydrogenation and does not form a semicarbazone and quinoxaline derivative; above



the m.p. it gives a substance oxidised by air to (II), obtained directly in 91% yield by CrO_3 . The prep. of 3:7-dimethyl-1:2-naphthaquinone is improved, as also is its condensation with $(CH_2.CMe)_2$ to 2:3:7:11-tetramethyl-1:4:11:12-tetrahydrophenanthraquinone; this forms normally a quinoxaline derivative, m.p. 137—138°, adds 2 H to give the 1:2:3:4:11:12- H_6 -derivative, m.p. 131°, and with H_2O_2 gives 2:4:5:4'-tetramethyl-1:2:3:6-tetrahydro-2:2'-diphenic acid, m.p. 248—249° (Me_2 ester, m.p. 88—89°; anhydride, m.p. 97—98°), converted at 330—333° by loss of CO_2 into 2:3:7:10-tetramethyl-1:4:10:11-tetrahydrofluorenone [semicarbazone, softens at 244°, m.p. 260° (decomp.)]. R. S. C.

Application of the diene synthesis to halogenated 1:2- and 3:4-phenanthrenequinones. L. F. FIESER and J. T. DUNN (J. Amer. Chem. Soc., 1937, 59, 1024—1028).—Chrysene- and 3:4-benzphenanthra-quinones are smoothly obtained by diene addition to halogenophenanthraquinones, followed by elimination of HCl and oxidation. Phenanthra-3:4-quinone and Br-AcOH give a dibromide, converted by hot H_2O into 2-bromophenanthra-3:4-quinone (I), m.p. 212—213° [corresponding quinol, m.p. 164—165.5° (Me_2 ether, m.p. 79—80°)], the structure of which is proved by conversion by $Ac_2O-H_2SO_4$ into 2-bromo-1:3:4-triacetoxypheanthrene, m.p. 195—196°, which by hydrolysis and aerial oxidation gives 2-bromo-3-hydroxyphenanthra-1:4-quinone, m.p. 198—199°; this quinone is stable to boiling dil. alkali and is unchanged by hot MeOH-HCl, which respectively degrade and methylate the Br-free OH-quinone. $(CH_2.CMe)_2$ adds to (I) in $CHCl_3$ at 100° (2 hr.), giving a Br-compound, converted by CrO_3 into 8:9-dimethylchrysene-5:6-quinone, m.p. 250—251°. Phenanthra-1:2-quinone (II) similarly yields the 3-Br-quinone (III), m.p. 245—246°, 3-bromo-1:2-dihydroxyphenanthrene, m.p. 195—196° (Me_2 ether, m.p. 82—83°), and 3-bromo-1:2:4-triacetoxypheanthrene, m.p. 188—189° [hydrolysed to an indefinite substance, m.p. 222° (decomp.)]. From (III) is obtained a 79% yield of 6:7-dimethyl-3:4-benzphenanthra-1:2-quinone, m.p. 194—195°, also obtained, but only in 29% yield, from (II). $(CH_2.CH)_2$ and (III) give 3:4-benzphenanthra-1:2-quinone, m.p. 190—191° (quinol, m.p. 194—195°), in 65% yield. 3-Phenanthrol and Cl_2 (excess) in AcOH at 13—17° give 1(or 2):4:4':9:10-pentachloro-3-keto-3:4:9:10-tetrahydrophenanthrene, m.p. 175—180° (decomp.), converted by many reagents into indefinite products, but by $SnCl_2-AcOH$ at room temp. into 1(or 2):4:9(or 10)-trichloro-3-phenanthrol, m.p. 130—131° (acetate, m.p. 164—165°), which with HNO_3-AcOH gives 1(or 2):9(or 10)-dichlorophenanthra-3:4-quinone, m.p. 239—240°, and with $Ac_2O-H_2SO_4$ yields 9(or 10)-chloro-1(or 2):3:4-triacetoxypheanthrene, m.p. 230—231°. R. S. C.

Two-step oxidation treated for the case of phenanthrenequinonesulphonate.—See A., I, 415.

Carbonyl constituents of eucalyptus oils. I. Occurrence of cryptal. P. A. BERRY, A. K. MACBETH, and T. B. SWANSON (J.C.S., 1937, 986—989).—l-4-isoPropyl- Δ^2 -cyclohexen-1-one (oxime, b.p. 160—161°/33 mm.) has been isolated from various eucalyptus oils, and on the evidence of oxidation, reduction, and identity of derivatives, is identical with "cryptal." It seems clear that the corresponding aldehyde (A., 1930, 602) has not been isolated from eucalyptus oils. F. R. S.

Supposed transformation of dihydroxydihydro- α -campholenic acid into pinonic acid. M. DELÉPINE (Bull. Soc. chim., 1937, [v], 4, 1145—1147).—The distillate from d-dihydroxydihydro- α -campholenic acid contains, not "pinonic acid," but d- α -campholonic acid, $[\alpha]_D +158^\circ$ in H_2O (semicarbazone, $[\alpha]_D +129^\circ$ in ammoniacal H_2O) (cf. this vol., 67). E. W. W.

Diene synthesis. III. Products obtained from α -terpineol by loss of water. K. ALDER and

H. F. RICKERT (Ber., 1937, 70, [B], 1364—1369).—The product obtained by the dehydration of α -terpineol is transformed by $\text{CO}_2\text{Et} \cdot \text{C} \cdot \text{CO}_2\text{Et}$ mainly into C_9H_{14} and *Et* 6-methyl-3-isopropylphthalate (I), b.p. 180—190°/15 mm., mixed with small amounts of a product (II), b.p. 196°/15 mm. Hydrolysis of (I) gives 6-methyl-3-isopropylphthalic anhydride, m.p. 102°, identified by oxidation to 3-methyl-6-hydroxyisopropylphthalic acid, m.p. 288°, and mellophanic acid. Probably (II) is a cycloheptadiene derivative (A) hydrogenated to a compound, $\text{C}_{14}\text{H}_{20}\text{O}_4$, m.p. 202—203° (decomp.). H. W.

Structure and probable biogenesis of β -caryophyllene. K. GANAPATHI (Current Sci., 1937, 5, 586).—The relationship of β -caryophyllene to orthodene by addition of an isoprene unit is discussed.

F. R. S.

Constitution of α -cyperone. A. E. BRADFELD, R. R. PRITCHARD, and J. L. SIMONSEN (J.C.S., 1937, 760—763).—The formula

$\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CHMe} \cdot \text{CO}$ (I) for α -cyperone (II) (A., 1936, 856) is abandoned in favour of

$\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$ (III). The hydrocarbon $\text{C}_{15}\text{H}_{18}$ from hydroxymethylene- α -cyperone is now identified as 1:3:7- $\text{C}_{10}\text{H}_5\text{Me}_2\text{Pr}^\beta$ (IV), which is synthesised (see below). The hydrocarbon from tetrahydroeremophilone and MgMeI followed by Se , previously regarded as (IV), is now identified as 1:5:7- $\text{C}_{10}\text{H}_5\text{Me}_2\text{Pr}^\beta$; the non-identity of the two hydrocarbons is thus no longer an argument against formula (III). A third formula,

$\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2$ (V), is excluded, since on this the action of O_3 on the semicarbazone of (II) would give a product $\text{C}_{14}\text{H}_{21}\text{O}_3\text{N}_3$, whereas the product obtained (*loc. cit.*) is $\text{C}_{15}\text{H}_{23}\text{O}_4\text{N}_3$, and is now formulated as

$\text{CHAc} \cdot \langle \text{CH}_2 \cdot \text{CH}_2 \rangle \cdot \text{CMe} \cdot [\text{CH}_2]_2 \cdot \text{CAc} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$. The acid from (II) and O_3 , previously regarded (*loc. cit.*) as $\text{C}_{13}\text{H}_{20}\text{O}_5$, dibasic (VI), is now formulated as $\text{CHAc} \cdot \langle \text{CH}_2 \cdot \text{CH}_2 \rangle \cdot \text{CMe} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$ (VII), and the supposed Me_2 ester of (VI) becomes the *Me* ester of (VII). The product from (II) and $\text{H}_2\text{O}_2 \cdot \text{NaOH}$, regarded as 6-acetyl-1-methyl-4-isopropenylcyclohexane-1-carboxylic acid, is renamed 1-methyl-4-isopropenylcyclohexan-2-one-1-propionic acid, the formation of which is an additional argument against formula (V).

Cuminaldehyde and $\text{CHMeBr} \cdot \text{CO}_2\text{Et} \cdot \text{NaOEt}$ give *Et* α -epoxy- β -cumyl- α -methylpropionate, b.p. 180—181°/24 mm., which is converted by $\text{KOH} \cdot \text{MeOH}$, and heating, into cuminyl *Me* ketone (VIII), b.p. 137°/22 mm. (semicarbazone, m.p. 142—143°; 2:4-dinitrophenylhydrazone, m.p. 137—138°), and $\alpha\beta$ -dihydroxy- β -cumyl- α -methylpropionic acid, decomp. 170—171°. With $\text{CH}_2\text{Br} \cdot \text{CO}_2\text{Et} \cdot \text{Zn} \cdot \text{C}_6\text{H}_6$, (VIII) yields *Et* β -cumylbutyrate, b.p. 170—174°/18 mm., which with

H_2SO_4 gives 3-methyl-7-isopropyl-1:2:3:4-tetrahydronaphthal-1-one, b.p. 165—173°/17 mm. (semicarbazone, decomp. 180—182°; 2:4-dinitrophenylhydrazone, m.p. 235—236°), methylated (MgMeI) and dehydrogenated (Se) to 1:3-dimethyl-7-isopropyl-naphthalene (see above), b.p. 165—167°/19 mm. [*picrate*, m.p. 102.5—104°; *s*- $\text{C}_6\text{H}_4(\text{NO}_2)_3$ derivative, m.p. 117—119—121°].

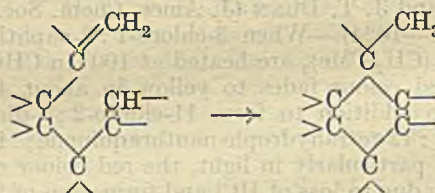
E. W. W.

Identity of α -dihydrophylocladene with iosene.

L. H. BRIGGS (J.C.S., 1937, 1035—1036).—Iosene (I) is identical with α -dihydrophylocladene. The C skeleton suggested for (I) is compatible with the Se dehydrogenation (*cf.* Soltys, A., 1929, 1429).

F. R. S.

Characterisation of basseol, a tetracyclic tri-terpene alcohol, and its isomerisation to β -amyrenol. J. H. BEYNON, I. M. HEILBRON, and F. S. SPRING (J.C.S., 1937, 989—991).—The fat from the bark of *Alstonia scholaris* contains no basseol (I), but mainly the amyrenols (chiefly β -) and lupeol. From the shea cambium, lupeol, α -amyrenol, and (I) have been isolated, but the yield of (I) is < that from the nut oil. The determination of the equiv. of basseol acetate and its isomerisation by various reagents to β -amyrenyl acetate lead to the formula $\text{C}_{30}\text{H}_{50}\text{O}$ for (I) (*cf.* Heilbron *et al.*, A., 1934, 1330). The acetate is hydrogenated to *bassenyl acetate*, m.p.



119—120°, $[\alpha]_D^{20} + 32.5^\circ$ in CHCl_3 , hydrolysed to basseol (benzoate, m.p. 156°, $[\alpha]_D^{19} + 48.1^\circ$ in CHCl_3), and gives CH_2O on ozonolysis. The ethylenic linkings of (I) are not conjugated and the reactive one is probably exocyclic. The isomerisation of (I) to β -amyrenol is formulated as above.

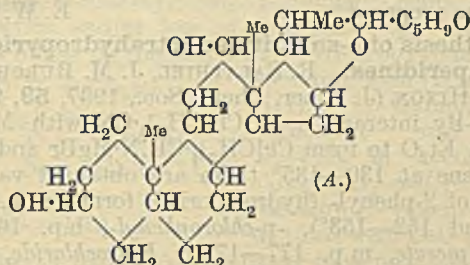
F. R. S.

Glycyrrhizin. III. Isomerism of glycyrrhetic acid. W. VOSS and G. BUTTER (Ber., 1937, 70, [B], 1212—1218; *cf.* this vol., 87).—The data, m.p. 253—255°, $[\alpha]_D^{21} + 159.1^\circ$ in EtOH , $+152^\circ$ in CHCl_3 , and m.p. 224.6—227° (*corr.*), $[\alpha]_D^{21} + 132.5^\circ$ in EtOH , $+124.6^\circ$ in CHCl_3 , are recorded for *Me* β - (I) and α - (II)-glycyrrhetate, respectively, obtained from varied sources and by differing processes. (I) and (II) are regarded as isomerides, not polymorphous forms (*cf.* Ruzicka *et al.*, *ibid.*, 202), since they are distinguished from one another by m.p., cryst. form, solubility, and $[\alpha]_D$ and the differences persist after crystallisation or sublimation. Reasons are advanced for considering that this isomerism persists through the aglucon to the glucoside and that glycyrrhizic acid is a mixture. The C skeleton of glycyrrhetic acid is discussed.

H. W.

Saponins and sapogenins. V. Oxidation products and structure of chlorogenin. C. R. NOLLER (J. Amer. Chem. Soc., 1937, 59, 1092—1094; *cf.* A., 1936, 1095).—Chlorogenin (I), m.p. 277—279°, and

$\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ in AcOH give a diketone (II), $\text{C}_{27}\text{H}_{40}\text{O}_4$, m.p. 247—248° after sintering at 236°, $[\alpha]_D^{25} - 69.6^\circ$ in dioxan [dioxime, m.p. 242—243°; with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives a substance, $\text{C}_{33}\text{H}_{46}\text{O}_3\text{N}_2$, m.p. 265—267° (rapid heating), 255—261° (slow heating)], and a ketodibasic acid, $\text{C}_{27}\text{H}_{40}\text{O}_7$, m.p. 235—237° (decomp.) after sintering, $[\alpha]_D^{25} - 42.8^\circ$ in dioxan (Me_2 ester, m.p. 158—159°, $[\alpha]_D^{25} - 39.1^\circ$, readily hydrolysed). Since the acid is probably not an α - or β -keto-acid, (I) is thus probably (A).



Digitonin does not ppt. (I), but (II) is reduced by Na-EtOH to a small amount of a substance, which is so pptd.; the configuration of $\text{C}_{(3)}$ is thus opposite to that in cholesterol.

R. S. C.

Toad poisons. VI. Constitution of Ch'an Su (Senso). M. KOTAKE and K. KUWADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 32, 1—3).—"Bufagin," previously described as obtained from senso (A., 1928, 1138), is shown by separation with CHCl_3 to be a mixture of cinobufagin (cf. Tschesche and Offe, A., 1936, 1516) and cinobufotalin, $\text{C}_{23}\text{H}_{32}\text{O}_6$, m.p. 248—249.5°, from which were prepared the Ac_2 , m.p. 219—220°, α -, m.p. 222—224° and β - H_4 -derivatives, m.p. 162—165°, and cinobufotalone, $\text{C}_{23}\text{H}_{28}\text{O}_6$, m.p. 246—248°. The H_4 -derivatives of bufagin previously described are shown to be hexahydrocinobufagins.

F. R. G.

Locoine.—See A., III, 309.

Constitution of cozymase.—See A., III, 313.

Cannizzaro reaction. V. M. RODIONOV and A. M. FEDOROVA (J. Gen. Chem. Russ., 1937, 7, 947—950).—Opianic acid, aq. CH_2O , and KOH or NaOH (55°; 12 hr.) give meconine in 93% yield. o -Hydroxymethylbenzoic acid or phthalide, and benzyl, anisyl, or furfuryl alcohols are prepared analogously from the appropriate aldehydes and CH_2O . R. T.

Constitution of the scoparoside (scoparin) of *Sarothamnus scoparius*, Koch. M. MASGRÉ and R. PARIS (Compt. rend., 1937, 204, 1581—1583).—Scoparin with boiling 10% KOH affords acetylvanillin; fermentative hydrolysis (rhamnodiastase of *Rhamnus utilis*) affords rhamnose and a flavin, scoparol, probably a Me ether of quercitol (cf. A., 1918, i, 503).

J. L. D.

Synthesis of 1:2-diphenylcoumarones. II. B. I. ARVENTI (Bull. Soc. chim., 1937, [v], 4, 999—1007; cf. A., 1936, 732).— o -Benzylphenol with BzCl and NaOH affords o -benzoyloxydiphenylmethane, b.p. 249°/18 mm., which is not converted into 1:2-diphenylcoumarone at 280—300°. The lactone of phenyl- β -1-hydroxynaphthylacetic acid with BzCl in Na_2CO_3 affords a compound converted at 250—270°,

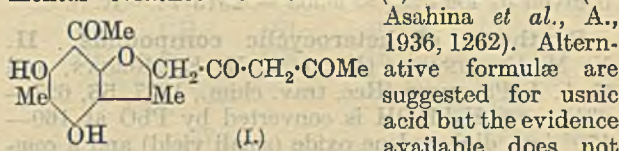
with liberation of gaseous products, into 1:2-diphenyl- α -naphthofuran (I), m.p. 100°, which with $\text{CrO}_3\text{-AcOH}$ at 60° gives 2:1- $\text{C}_{10}\text{H}_8\text{Bz.OBz}$, m.p. 163° (lit., 154°), hydrolysed (NaOH) to 2:1- $\text{C}_{10}\text{H}_8\text{Bz.OH}$. The lactone of phenyl- o -tolylacetic acid gives a Bz derivative which at 270—280° is converted into 1:2-diphenyl-6-methylcoumarone, m.p. 64—65°. 1:2-Diphenyl-4-methylcoumarone (cf. A., 1936, 732) with excess of CrO_3 gives a mixture of 2-benzoyloxy-5-methylbenzophenone and m -benzoyl- p -benzoyloxybenzoic acid; milder oxidation yields only the former (cf. A., 1936, 997). Prepared similarly to (I), 1:2-diphenyl-4:5- and -4:6-dimethylcoumarone have m.p. 143° and 128—129°, respectively. All these coumarones afford coloured solutions in conc. H_2SO_4 .

J. L. D.

Walder's "dinaphthyl," 1:1'-dinaphthyl, and the ultra-violet absorption of β -dinaphthylene oxide. K. BRASS and R. PATZELT (Ber., 1937, 70, [B], 1349—1353).—The "1:1'-dinaphthyl" of Walder (A., 1883, 208), obtained by the distillation of β -dinaphthol (I) with Zn dust, is shown to be β -dinaphthylene oxide, identical with that obtained from (I) and P_2O_5 . 1:1'-Dinaphthyl (II) cannot be obtained by distilling (I) with Zn dust and is best obtained from 1- $\text{C}_{10}\text{H}_7\text{I}$. (II) appears unable to add picric acid.

H. W.

Usnic acid. V. F. H. CURD and A. ROBERTSON (J.C.S., 1937, 894—901).—Usnic acid and 96% EtOH heated under pressure (cf. Widman, A., 1903, i, 96) give decarbusnic acid (I), m.p. 178—179° (pyrazole derivative, m.p. 237—238°, regarded by Widman as a hydrazone), and deacetylcarbusnic acid (II), m.p. 199—200° (Ac_2 derivative, m.p. 146—147°). Hydrolysis (KOH) of (I) affords AcOH, COMe_2 , usnetic and pyrousnetic acids, and (II). The experimental evidence for formula (I) is discussed (cf.



Asahina *et al.*, A., 1936, 1262). Alternative formulæ are suggested for usnic acid but the evidence available does not permit a decision. The formation of decarbusnol by dehydration of (I) with conc. H_2SO_4 and the isomerisation of usnic acid to usnic acid (III) with H_2SO_4 have been confirmed. Decarboxylation of (III) yields decarbusnol and indicates that the C atom lost in degradation of usnic acid to (I) appears as the CO_2H of (III).

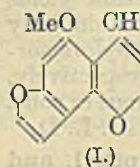
F. R. S.

Preparation of halogenated derivatives of dihydroxydiphenylene dioxide. J. FREJKA, B. SEFRANEK, and J. ZIKA (Coll. Czech. Chem. Comm., 1937, 9, 238—246).—Tetrachloropyrocatechol with NaNO_2 and AcOH affords 1:4:5:6:7:8-hexachlorodiphenylene dioxide 2:3-quinone, m.p. 288.5°, reduced (Sn-HCl or SO_2) to 1:4:5:6:7:8-hexachloro-2:3-dihydroxydiphenylene dioxide, m.p. 276° (decomp.) (diacetate, m.p. 300—301°). Similarly, 4:5-dichloropyrocatechol affords 6:7-dichlorodiphenylene dioxide 2:3-quinone, reduced (Sn-HCl) to 6:7-dichloro-2:3-dihydroxydiphenylene dioxide (diacetate, m.p. 218°), and from tetrabromopyrocatechol are prepared 1:4:5:6:7:8-hexabromodiphenylene

dioxide 2:3-quinone and 1:4:5:6:7:8-hexabromo-2:3-dihydroxydiphenylene dioxide [diacetate, m.p. > 300° (decomp.)]. 4-Chloropyrocatechol (improved prep.) with $\text{NaNO}_2\text{-AcOH}$ affords 4'-(4-chloro-2-hydroxy-phenoxy)-1':2'-benzoquinone, reduced (SO_2) to 4'-(4-chloro-2-hydroxyphenoxy)pyrocatechol (triacetate, m.p. 178°). J. D. R.

Natural coumarins. XXX. Synthesis of bergaptol and of isobergaptol. E. SPATH and G. KUBICZEK (Ber., 1937, 70, [B], 1253—1255).—

3:4:6-Triacetoxycoumaran is condensed with Et sodioformylacetate and the product, after acidification, is distilled, thus giving *allobergaptol* and *bergaptol*, m.p. 276—278° (vac.). The latter substance is partly methylated and then distilled, thereby giving *isobergaptol* (I), m.p. 224° (vac.), identical with the natural product. H. W.



Natural coumarins. XXXI. Constitution of ammosesinol. E. SPATH and F. KESZTLER (Ber., 1937, 70, [B], 1255—1258).—Mainly a reply to Raudnitz (this vol., 204). The substance obtained by oxidation of diacetylhexahydroammosesinol and decarboxylation of the product is identified as 86 μ -trimethyl-*n*-tetradecoic acid by analyses and comparison of its *p*-xenylamide, m.p. 101—102°, with that of the synthetic acid derived from farnesol. $\gamma\lambda$ -Trimethyl-*n*-trideco-*p*-xenylamide has m.p. 94.5—95.5°. H. W.

Principal optical and physical properties of the carbon tetrachloride solvate of rotenone. E. L. GOODEN and C. M. SMITH (J. Amer. Chem. Soc., 1937, 59, 787—789).—Crystallo-optical data are recorded for the rotenone- CCl_4 compound. It has d^{30}_{20} 1.40. The dissociation pressure from 60° to 90° is given by $\log P_{\text{mm.}} = 9.308 - 2313/T$. R. S. C.

Synthesis of heterocyclic compounds. II. N. M. CULLINANE, (MISS) N. M. E. MORGAN, and C. A. J. PLUMMER (Rec. trav. chim., 1937, 56, 627—631).— $\text{o-C}_6\text{H}_4\text{Ph}\cdot\text{OH}$ is converted by PbO at 160—170° into diphenylene oxide (small yield) and a compound, m.p. 194°. Thianthren and Cu-bronze in H_2 afford diphenylene sulphide. Diphenylene selenide is obtained from diphenylene sulphone and Se and the diselenide similarly from the corresponding disulphone obtained by oxidising thianthren with CrO_3 in boiling AcOH . Production of a four-membered ring appears more difficult. Diphenylene is not obtained from $\text{o-C}_6\text{H}_4\text{Ph}\cdot\text{OH}$ and P_2O_5 , 50% or conc. H_2SO_4 , whilst when 70% H_2SO_4 is used the product is the *sultone*, $\text{C}_6\text{H}_4\langle\text{SO}_2\rangle\text{O}$, m.p. 110°. PhOBz is transformed by AlCl_3 into $\text{o-C}_6\text{H}_4\text{Bz}\cdot\text{OH}$, m.p. 41°, which passes into xanthone, PhOH , and BzOH when heated at 280°. H. W.

Condensation of chlorohydrins with piperidine. C. VASSILIADIS (Bull. Soc. chim., 1937, [v], 4, 1131—1136).—Piperidine (I) (2 mols.) and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ (1 mol.) in COMe_2 give β -piperidinoethyl alcohol (II), b.p. 90°/12 mm., of which the hydrochloride, m.p. 64—65°, is obtained when only 1 mol. of (I) is used, in PhMe . With BzCl , (II) gives β -

piperidinoethyl benzoate hydrochloride, m.p. 167—168°. Similarly obtained is β -piperidinoethyl *p*-nitrobenzoate hydrochloride, m.p. 175—176°, reduced ($\text{NHPh}\cdot\text{NH}_2$) to the *p*-aminobenzoate hydrochloride, m.p. 88—90° (dihydrochloride, decomp. 208—235°). With $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$, (I) (4 mols.) yields *s*-dipiperidinoisopropyl alcohol, b.p. 172—173°/12 mm., of which the dihydrochloride (III), m.p. 209—210°, is obtained when only 2 mols. of (I) are used. The benzoate, m.p. 240°, and *p*-nitrobenzoate, m.p. 220—235°, of (III) are prepared. E. W. W.

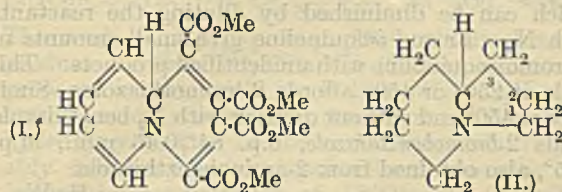
Synthesis of α -substituted tetrahydropyridines and piperidines. R. SALATHIEL, J. M. BURCH, and R. M. HIXON (J. Amer. Chem. Soc., 1937, 59, 984—986).—By interaction of $\text{Cl}\cdot[\text{CH}_2]_4\cdot\text{CN}$ with MgRX first in Et_2O to form $\text{Cl}\cdot[\text{CH}_2]_4\cdot\text{CR}\cdot\text{N}\cdot\text{MgBr}$ and then in xylene at 130—135° there are obtained varying yields of 2-phenyl- (hydrochloride, forms, m.p. 86—87° and 152—153°), *p*-chlorophenyl-, b.p. 165°/13 mm. (picrate, m.p. 177—178°; hydrochloride, m.p. 215—217°; HgCl_2 double salt, m.p. 133—135°), *p*-tolyl-, b.p. 145°/13 mm. (platini-, m.p. 186—187°, and hydrochloride, $+\text{H}_2\text{O}$, m.p. 137—137.5°, and anhyd., m.p. 175—177°; HgCl_2 double salt, m.p. 119.5°; picrate, m.p. 178—179°), -cyclohexyl-, b.p. 118—125°/17 mm. (hydrochloride, m.p. 222—224°), and -*n*-butyl-tetrahydropyridine, b.p. 195—200° (hydrochloride, unstable; platinichloride, m.p. 156°), reduced by Sn-HCl to 2-phenyl-, *p*-chlorophenyl-, b.p. 145°/8 mm., m.p. 16° (hydrochloride, m.p. 259—260°), *p*-tolyl-, b.p. 135°/8 mm. (hydrochloride, m.p. 209—210°), -cyclohexyl-, b.p. 135°/35 mm. (hydrochlorides, m.p. 197—198° and 250°), and -*n*-butyl-piperidine, b.p. 185—192° (hydrochloride, m.p. 185—186°). R. S. C.

Action of hypiodite on some pyridinium bases. P. KARRER, F. SCHLENK, and H. VON EULER (Arkiv Kemi, Min., Geol., 1937, 12, B, No. 26, 5 pp.).—Cozymase, glucosido-1-pyridinium bromide, and nicotinamide methiodide absorb approx. 6.5, 8, and 7.5 atoms of I, respectively, from alkaline solution. F. N. W.

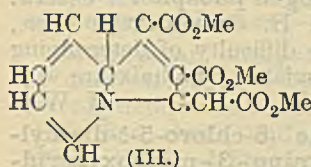
Neutral substances formed in Tschitschibabin's β -collidine synthesis. Reply to Hunteberg. A. E. TSCHITSCHIBABIN (J. pr. Chem., 1937, [ii], 148, 266).—Hunteberg's results (A., 1936, 612) are in line with those of Tschitschibabin. C_6H_6 is the only recognisable substance among the products obtained from PhCHO and Al_2O_3 at 400—450°. R. S. C.

Syntheses in the hydroaromatic series. XXVII. Diene syntheses of hetero-rings containing nitrogen. XII. Decomposition of the "yellow substance" to an isomeride of norlupinane (1-methyloctahydroindolizine). O. DIELS and H. SCHRUM. XIII. α -Picoline and acetylenedicarboxylic ester. O. DIELS and H. PISTOR (Annalen, 1937, 530, 68—86, 87—98; cf. A., 1935, 1389).—XII. The stable "yellow substance," obtained from $\text{C}_5\text{H}_5\text{N}$ and $(\text{C}\cdot\text{CO}_2\text{Me})_2$ (A., 1934, 782), is probably Me_4 quinolizine-1:2:3:4-tetracarboxylate (I). Its hydrolysis leads to partial loss of CO_2 and a multiplicity of products; all the bases obtained therefrom by decarboxylation and reduction are

related to octahydroindolizine (II); the acids are colourless and melt at lower temp. than does (I);



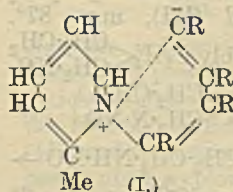
therefore, probably, ring-crumpling occurs during hydrolysis and/or loss of CO_2 and, e.g., the ester which might be the Me_3 1:2:4-tricarboxylate corresponding with (I) is really (III). (?) Quinolizinedicarboxylic acid and H_2 -PtO₂ in AcOH give slowly a H_4 -acid, m.p. 218° (decomp.), which, when distilled with CaO gives a



mixture of bases, hydrogenated to a mixture of (II) and 1-methyloctahydroindolizine (IV), b.p. 168—169°/760 mm. (picrate, m.p. 193°; *aurichloride*, m.p. 145—146°; *methiodide*, m.p. 311—312°); identification of (IV) is effected by direct comparison with the synthetic base (cf. Ochiai *et al.*, A., 1934, 901) and by degradation. BrCN converts (IV) into 2-*n*-butylpiperidine, b.p. 188—190°/764 mm. (*hydrochloride*, m.p. 185°; impure picrolonate, m.p. 204°; *aurichloride*, an oil), which is obtained (*picrolonate*, m.p. 184—186°) also by reaction of Li α -picolinyl with Pr^nBr and hydrogenation of the product; the difference in the m.p. of the picrolonates is believed to be due to the BrCN-fission having occurred to a small extent in the piperidine ring, leading to formation of some 2-methyl-6-*n*-butylpyrrolidine. Bases, which might have been formed by BrCN-fission of (IV), were synthesised for comparison. PhLi and 2-picoline give Li α -picolinyl, which with Pr^nBr gives a base, hydrogenated to 2-isopropylpiperidine (*hydrochloride*, m.p. 205—206°). 2-*tert*-Butylpiperidine *hydrochloride* has m.p. 188—189°. PrCOCl , Et 2-methylpyrrole-3-carboxylate, and AlCl_3 give Et 2-methyl-5-butyrylpyrrole-3-carboxylate, hydrolysed to the corresponding *acid*, m.p. 242° (decomp.), which at 300—320° gives 2-methyl-5-butyrylpyrrole, m.p. 88—89, converted (N_2H_4 -NaOEt) into 2-methyl-5-*n*-butylpyrrole, b.p. 100—102°/13 mm., and thence by NH_2OH into β -*oximinononane*, m.p. 119—120°, or by H_2 -PtO₂ into 2-methyl-5-*n*-butylpyrrolidine, b.p. 177—179°/765 mm. (*picrolonate*, m.p. 215—217°; *aurichloride*, an oil; *hydrochloride*, m.p. about 98—103°). NaNH_2 , BuCO_2Et , and COMeBu^n give *undecane- ϵ -dione*, b.p. 110—123°/14 mm., which with $\text{OH}^-\text{N}:\text{CAc}:\text{CO}_2\text{Et}$ and Zn-AcOH gives Et 3-methyl-5-butyl-4-valerylpyrrole-2-carboxylate, m.p. 75—76°, converted by $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ (3:2) into 3-methyl-5-*n*-butylpyrrole. 2-Butyrylpyrrole (modified prep.) with $\text{N}_2\text{H}_4\text{-NaOEt}$ at 160—170° gives 2-*n*-butylpyrrole, b.p. 80—81°/11—12 mm., which gives (Grignard; ClCO_2Et) Et 2-*n*-butylpyrrole-5-carboxylate, b.p. 150—160°/10—11 mm.; this gives (HCN-HCl-CHCl_3) the 3- (or 4)-aldehyde, m.p. 55—57°, reduced ($\text{N}_2\text{H}_4\text{-NaOEt}$) to 3- (or 4)-methyl-2-*n*-butylpyrrole, b.p. 91°/10—11 mm., hydro-

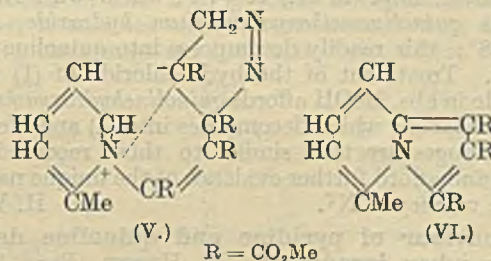
genated to 3- (or 4)-methyl-2-*n*-butylpyrrolidine, b.p. 180° (*hydrochloride*, m.p. about 100°; *aurichloride*, m.p. 95—96°).

XIII. $(\text{C}:\text{CO}_2\text{Me})_2$ condenses with 2-picoline only in the dimeric form; it reacts partly at the N to give the "unstable" product (I) and partly at the Me to give $\beta\gamma\delta\epsilon$ -tetracarboxymethoxy- Δ^{88} -pentadienylpyridine (II); "stabilisation" of (I) occurs at the CH and not at the Me, the sole product from (I) being the "stable adduct," Me_4 1-methylquinolizine-5:6:7:8-tetracarboxylate (III). Structures are proved by the reactions described below. (II), m.p. 126°, does not



react with CH_2N_2 , is red, but gives colourless salts with acids, is hydrogenated (PtO_2) in EtOAc (not colloidal Pd in MeOH) to 2- $\beta\gamma\delta\epsilon$ -tetracarboxymethoxyamylpyridine, m.p. 132°, gives a Br_3 -derivative, m.p. 126°, and, when evaporated in MeOH, loses

MeOH by ring-closure to 2-6'-hydroxy-2':3':4'-tricarboxymethoxyphenylpyridine (IV), m.p. (anhyd.) 128°, (+ H_2O) 95—105° (deep red FeCl_3 colour; *phenylurethane*, m.p. 148°; *Br*-derivative, m.p. 133°); when boiled with AcOH, (I) gives an *acid*, $\text{C}_{13}\text{H}_{10}\text{O}_3\text{N}(\text{OMe})_2\cdot\text{CO}_2\text{H}$, +0.5 H_2O , m.p. 208° (decomp.), which gives a brownish-red FeCl_3 colour, gives an indigo-blue compound with Ac_2O , and with CH_2N_2 yields the *Me ether*, m.p. 136° (decomp.), of (IV). (I), m.p. 135°, yellow, with CH_2N_2 gives the yellow *adduct* (V), m.p. 125° (decomp.), gives a *dibromide*, m.p. 187° (decomp.), which does not react with CH_2N_2 , and, when boiled for a long time in AcOH, gives (III), yellow, m.p. 234° (decomp.).



H_2O_2 converts (III) into 2-picoline-6-carboxylic acid *N*-oxide, m.p. 177° (synthesis from 2:6-dimethylpyridine described). $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ oxidises (III) with ring-crumpling to the colourless *indolizine ester* (VI), m.p. 116°, also obtained by the action of dil. Na_2CO_3 on the *N*-tribromide, m.p. 135° (decomp.), of (III). R. S. C.

Fission of tertiary amines by nitrous acid.

II. Synthesis of β -*o*-carboxyphenylethylamines. R. WEGLER and W. FRANK (Ber., 1937, 70, [B], 1279—1287; cf. A., 1936, 1373).—Treatment of 1-alkylpiperidines with HNO_2 results in elimination of the alkyl group and formation of 1-nitrosopiperidine. With the 1-octyl compound the action proceeds with difficulty but in no case is there any evidence of opening of the piperidine ring. *cyclohexylamine* (I), $\text{o-C}_6\text{H}_4(\text{CH}_2\text{Br})_2$, and powdered NaOH in PhMe at 200° give 2-cyclohexyl-1:3-dihydroisindole, b.p. 112°/0.2 mm., m.p. 64°, converted by $\text{NO}_2 + \text{O}_2$ in AcOH at 80—90° into *cyclohexylphthalimide*, m.p. 167°,

also obtained from (I) and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ at 170° and reduced by Sn and HCl in AcOH to cyclohexylphthalimidine, m.p. $109\text{--}110^\circ$. 2-Benzoyltetrahydroisoquinoline and $\text{NO}_2 + \text{O}_2$ in AcOH at $70\text{--}90^\circ$ give BzOH. 2-isoAmyltetrahydroisoquinoline, NaNO_2 , and AcOH give a substance, $\text{C}_{14}\text{H}_{20}\text{O}_3\text{N}_2$, b.p. $192^\circ/16\text{ mm.}$, indicating the fission of the ring. Oxidation of tetrahydroisoquinoline by NO_2 in AcOH at $>70^\circ$ affords the lactone (II), $\text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO--O} \end{smallmatrix}$, b.p. $165^\circ/16\text{ mm.}$, transformed by very cautious treatment with NaOH followed by H_2SO_4 into $o\text{-}\beta\text{-hydroxyethylbenzoic acid}$ (III), m.p. 87° . The course of the change is probably $\text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{NH} \end{smallmatrix} \rightarrow \text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO--NH} \end{smallmatrix}$ (or $\text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{N--NO} \end{smallmatrix}) \rightarrow \text{C}_6\text{H}_4\text{--}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO--N--NO} \end{smallmatrix} \rightarrow \text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NO} \rightarrow$ (III) \rightarrow (II). Addition of (III) to SOCl_2 at $<-3^\circ$ followed by heating of the mixture at 80° yields $o\text{-}\beta\text{-chloroethylbenzoyl chloride}$, b.p. $135^\circ/15\text{ mm.}$, converted by NHEt_2 under differing conditions into $o\text{-}\beta\text{-diethylaminoethylbenzdiethylamide}$, b.p. $190^\circ/16\text{ mm.}$ (hydrochloride, m.p. 168° after softening at 155°), or $o\text{-}\beta\text{-chloroethylbenzdiethylamide}$; the latter with NH_2Me affords $o\text{-}\beta\text{-methylaminoethylbenzdiethylamide}$, b.p. $182^\circ/15\text{ mm.}$, and the compound $\text{NMe}(\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NEt}_2)_2$, b.p. $230^\circ/\text{high vac.}$ (hydrochloride). H. W.

Methiodide of quinoline 1-oxide. M. HENZE (Ber., 1937, 70, [B], 1270—1273).—Quinoline 1-oxide (I) is converted by MeI into the very hygroscopic methiodide, m.p. (indef.) $70\text{--}75^\circ$, which with NaOH affords quinolinemethoxyammonium hydroxide, m.p. $66\text{--}68^\circ$; this readily decomposes into quinoline and CH_2O . Treatment of the hydrochloride of (I) with NaOMe in abs. MeOH affords quinolinemethoxyammonium methoxide, which decomposes into (I) and MeOH. The changes are thus similar to those recorded for NMe_3 and afford further evidence of the unique nature of one valency of N^\vee . H. W.

Behaviour of pyridine and quinoline derivatives when irradiated. M. HENZE (Ber., 1937, 70, [B], 1273—1274).—Treatment of 2-methylquinoline with PhCHO and ZnCl_2 or Ac_2O gives benzylidenequinaldine (I) and benzylidenediqualdine (hydrochloride, m.p. $150\text{--}155^\circ$; platinichloride, decomp. 260°). Exposure of (I) as solid or in C_6H_6 to sunlight leads to the dimeride, $\text{C}_9\text{H}_6\text{N}\cdot\text{CH}\begin{smallmatrix} \text{CHPh} \\ \text{CH}(\text{C}_6\text{H}_5\text{N}) \end{smallmatrix}\text{CHPh}$, m.p. 198° after subliming at 180° (picrate, m.p. $228\text{--}230^\circ$). Attempts to dimerise the corresponding $\text{C}_5\text{H}_5\text{N}$ derivative or to obtain compounds of the truxillic acid type by irradiation of pyridyl- or quinolyl-acrylic acids were unsuccessful. H. W.

Bromination of quinoline, isoquinoline, thiazole, and benzthiazole in the gaseous phase. H. E. JANSEN and J. P. WIBAUT (Rec. trav. chim., 1937, 56, 699—708).—Bromination of quinoline at 300° gives 3-bromoquinoline in $>25\%$ yield whereas at $450\text{--}500^\circ$ the main product is 5-bromoquinoline (yield $50\text{--}60\%$). The influence of temp. therefore, is similar to that observed with $\text{C}_5\text{H}_5\text{N}$. In both

cases small amounts of unidentified dibromoquinolines are produced. Considerable carbonisation is observed, which can be diminished by diluting the reactants with N_2 . Br and isoquinoline give small amounts of 1-bromoisoquinoline with unidentified products. Thiazole at 250° or 450° affords 2-bromothiazole. Similarly at 450° and without dilution with N_2 benzthiazole yields 2-bromobenzthiazole, b.p. $84^\circ/0.45\text{ mm.}$, m.p. 39.5° , also obtained from 2-aminobenzthiazole.

H. W.

Manufacture of acid amides substituted at the nitrogen atom [quinolines].—See B., 1937, 652.

Acridine salts of hydrogen phosphoric esters. T. WAGNER-JAUREGG and H. GRIESSHABER (Ber., 1937, 70, [B], 1458).—The difficulty of determining C in these compounds is obviated by admixture with V_2O_5 . H. W.

Synthesis of acriquinine (8-chloro-5- δ -diethylamino- α -methylbutylamino-3-methoxyacridine). O. J. MAGIDSON, A. M. GRIGOROVSKI, V. I. MAXIMOV, and R. S. MARGOLINA (Chim. Farm. Prom., 1935, No. 1, 26—34).—Two stages in the synthesis are described, viz., (i) $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2 \rightarrow 1:2:4\text{-C}_6\text{H}_3\text{MeCl}\cdot\text{NO}_2 \rightarrow$ the amine $\rightarrow 1:2:4\text{-C}_6\text{H}_3\text{MeCl}_2 \rightarrow 2:4\text{-C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{H} + \text{anisidine} \rightarrow N\text{-}p\text{-anisyl-4-chloroanthranilic acid} \rightarrow 5:8\text{-dichloro-3-methoxyacridine (I)}$, and (ii) $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl} \rightarrow \text{NEt}_2\cdot[\text{CH}_2]_3\cdot\text{Ac} \rightarrow$ the oxime $\rightarrow \text{NEt}_2\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{NH}_2$ (II). Acriquinine is formed by (acid or alkali) condensation of (I) and (II).

CH. ABS. (p)

Reactions of 2-bromo- and 3-bromo-quinoline. H. E. JANSEN and J. P. WIBAUT (Rec. trav. chim., 1937, 56, 709—713).—2-Bromoquinoline (I) is only slowly affected by warm liquid NH_3 but in presence of Cu powder at 70° 2-aminoquinoline, m.p. 129° , is obtained in 50% yield. KCN and (I) in $\text{EtOH-H}_2\text{O}$ at 200° yield only carbostyryl. When distilled with CuCN (I) gives 2-cyanoquinoline (II), m.p. 94° (yield 63%). Towards $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (I) behaves in the same manner as does 2-chloroquinoline. K pyrrole and (I) in C_6H_6 at 160° afford 2-2'-pyrrolylquinoline, m.p. 129° , in 40% yield. 3-Bromoquinoline (III) and Cu powder in liquid NH_3 at 70° give 3-aminoquinoline, m.p. $83\text{--}84^\circ$, in 60% yield. 3-Cyanoquinoline, m.p. 107° , is obtained from (III) and CuCN. Hydrogenation (Pd in 80% EtOH containing HCl) of (II) yields 2-quinolylmethylamine (dihydrochloride, m.p. about 240°). K pyrrole, $\text{CHNa}(\text{CO}_2\text{Et})_2$, or Mg did not react with (III). H. W.

Structure of benzamidine-glyoxal and of its compounds with aromatic aldehydes. J. B. EKELEY and A. R. RONZIO (J. Amer. Chem. Soc., 1937, 59, 1118—1121).—Absorption spectra support the open-chain formula for the additive products of aromatic amidines with glyoxal and of $\text{NH}_2\cdot\text{CPh}\cdot\text{NH}$ with Ac_2 , and indicate that amidines, glyoxal, and aldehydes condense thus: $\text{RCHO} + (\text{CHO})_2 \rightarrow \text{RCO}\cdot\text{CH}(\text{OH})\cdot\text{CHO} + \text{NH}_2\cdot\text{CR}'\cdot\text{NH} \rightarrow \text{RCO}\cdot\text{CH}\begin{smallmatrix} \text{CH}\cdot\text{N} \\ \text{N}=\text{CR}' \end{smallmatrix} \text{ (A)} \rightleftharpoons \text{OH}\cdot\text{CR}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{N} \\ \text{N}=\text{CR}' \end{smallmatrix} \text{ (B)}$, (A) existing in acid or neutral and (B) in alkaline solution. The product from $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is coloured in acid solution and thus probably

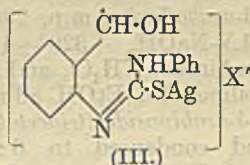
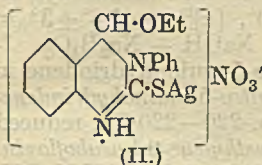
exists as (B) in alkaline, as (A) in neutral, but as $\text{Cl}(\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C} \begin{smallmatrix} \text{CH:N} \\ \text{NH-CPh} \end{smallmatrix})$ in acid, solution.

The acid, $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_2$, m.p. 255° , obtained as by-product in the $\text{NH}_2 \cdot \text{CPh} \cdot \text{NH} \cdot (\text{CHO})_2$ reaction, is prepared in 75% yield by adding $\text{CHO} \cdot \text{CO}_2\text{H}$ to the main reaction product, and, since it resembles phenyl-hydroxypyrimidine in absorption spectrum, is probably 5-hydroxy-2-phenylpyrimidine-4-carboxylic acid, formed by condensation of $(\text{CHO})_2$ and $\text{CHO} \cdot \text{CO}_2\text{H}$ to $\text{CO}_2\text{H} \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{CHO}$ before reaction with $\text{NH}_2 \cdot \text{CPh} \cdot \text{NH}$.

R. S. C.

Manufacture of compounds of the anthracene series [pyrimidones].—See B., 1937, 653.

Heteropolar compounds. III. Argenti-salts of derivatives of 4-hydroxy-2-thion-1:2:3:4-tetrahydroquinazoline. (MILE.) L. MANOLESCU (Bull. Soc. chim., 1937, [v], 4, 1126—1131; cf. A., 1935, 1253).—4-Ethoxy-2-thion-3-phenyltetrahydroquinazoline (I) with AgNO_3 in EtOH gives Ag 4-ethoxy-2-thiol-3-phenyl-3:4-dihydroquinazolinium nitrate (II), m.p. 183° , which with acids in Et_2O or EtOH yields salts (III) of Ag 4-hydroxy-2-thiol-3-

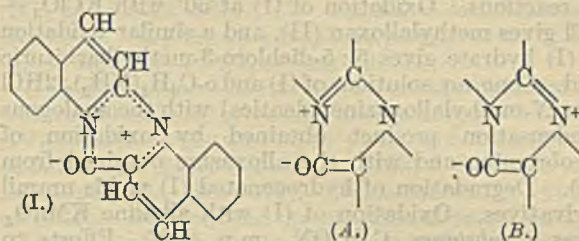


phenyl-3:4-dihydroquinazoline; the perchlorate, m.p. 227° , hydrochloride, m.p. $175\text{--}177^\circ$, hydrobromide, m.p. $161\text{--}162^\circ$, and hydroiodide, m.p. $165\text{--}166^\circ$, are described, in coloured and colourless forms. 4-Ethoxy-2-thion-3-allyl- and -3-*o*- and -*p*-tolyl-tetrahydroquinazoline give only Ag 4-ethoxy-2-thiol-3-allyl-, m.p. 140° , -3-*o*-tolyl-, decomp. 173° , and -3-*p*-tolyl-3:4-dihydroquinazoline, decomp. $180\text{--}182^\circ$. The 6-Br-derivative of (I) gives Ag 6-bromo-4-hydroxy-2-thiol-3-phenyl-3:4-dihydroquinazolinium nitrate, decomp. 180° .

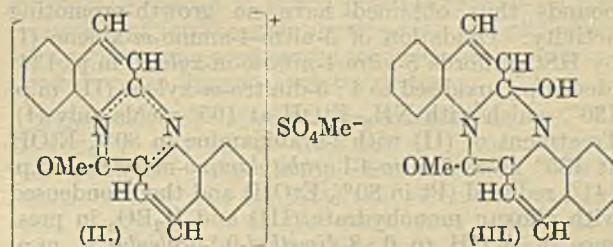
E. W. W.

Dyes from quinaldic and isoquinaldic acid. F. KROLLFEIFFER and K. SCHNEIDER (Annalen, 1937, 530, 34—50).—Besthorn's dye (I), $\text{C}_{19}\text{H}_{12}\text{ON}_2$ (A., 1904, i, 527), is obtained without intermediate products from quinaldoyl chloride, quinoline, and NaCN, NaOH, or NaOAc in aq. COMe_2 or Et_2O , and by addition of BzCl to quinoline and quinaldic acid in hot C_6H_6 . Quinoline-2-carboxylic anhydride, sinters at 100° , m.p. about $245\text{--}250^\circ$, is obtained by shaking the acid chloride in Et_2O with aq. $\text{C}_5\text{H}_5\text{N}$, NaOAc, NaHCO_3 , or Na quinaldate; it yields the amide and anilide, m.p. $138\text{--}139^\circ$, normally, but gives (I) when heated. With hot H_2O or MeOH it is partly hydrolysed and partly converted into (I) by loss of CO_2 ; it is stable when pure, but, when impure, yields (I) if kept. Formulae hitherto ascribed to (I) are incorrect. It is unimol. (cryoscopy in PhNO_2 ; ebullioscopy in Ac_2O and NH_3Ph); it is not a free radical, since it does not react with dry O_2 or N_2O and is diamagnetic ($\chi \times 10^6 = -0.65$ at 20° , -0.9 ± 0.05 at -183°); its absorption (detailed) in C_6H_6 and EtOH differs only in the position of the band; the annexed formula is, therefore,

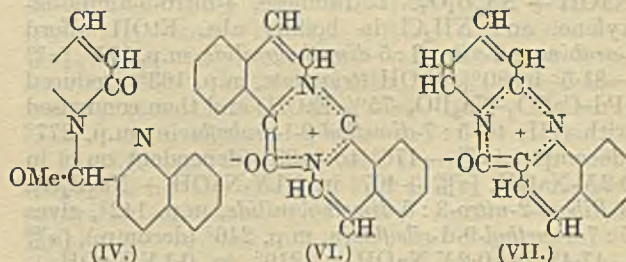
assigned; the formulation of the central ring is intended to denote mesomerism (Ingold) (or resonance) between (A) and (B). Hot Me_2SO_4 and (I) rapidly



give the yellow salt (II), m.p. $179\text{--}180^\circ$ (decomp. from 170°); with warm aq. NaOH this gives first a clear solution, then gives a red oil, which is sol. in dil. HCl and is thus the hydroxide corresponding with (II), and on longer heating partly regenerates (I) and partly gives a colourless substance, m.p. $213.5\text{--}214.5^\circ$, which contains labile OMe and with hot 48% HBr



slowly gives carbostyryl and quinoline-2-aldehyde and is thus (III) or, less probably, (IV). When isoquinaldic [isoquinoline-1-carboxylic] acid (V) (prep. modified to give a 60% yield) is boiled in Ac_2O , or when it and its chloride are treated with BzCl in C_6H_6 , the orange-red dye, $\text{C}_{19}\text{H}_{12}\text{ON}_2$ (VI), m.p. about



280° (decomp. from 100°), is formed; this regenerates (V) and isoquinoline when boiled with 48% HBr, and gives with Me_2SO_4 an ether salt, m.p. $205\text{--}208^\circ$ (decomp.), analogous to (II), which regenerates the dye with hot NaOH. $\text{C}_5\text{H}_5\text{N}$ (2 mols.) and quinaldoyl chloride (1 mol.) in hot C_6H_6 give the brownish-red dye, $\text{C}_{15}\text{H}_{10}\text{ON}_2$ (VII), $+0.5\text{H}_2\text{O}$, m.p. $238\text{--}240^\circ$ (decomp.), converted by HBr into quinaldic acid and $\text{C}_5\text{H}_5\text{N}$, and by Me_2SO_4 into the Me ether methosulphate, m.p. $165\text{--}168^\circ$ (decomp.; sinters at 150°), analogous to (II), which yields the corresponding methiodide, decomp. about 190° after sintering, and methopicate, m.p. $193\text{--}194^\circ$, and with NaOH partly regenerates the dye.

R. S. C.

Constitution of toxoflavin. A. G. VAN VEEN and J. K. BAARS (Proc. K. Akad. Wetensch. Amsterdam, 1937, 40, 498—505; cf. A., 1934, 537).—

Toxoflavin (I), $C_6H_6O_2N_4$, is considered to be $NMe \cdot CO \cdot C \cdot N > CH_2$, which is in agreement with all its reactions. Oxidation of (I) at 50° with $KClO_3 + HCl$ gives methylalloxan (II), and a similar oxidation of (I) hydrate gives 5:5-dichloro-3-methylbarbituric acid. Conc. aq. solutions of (I) and $o\text{-}C_6H_4(NH_2)_2 \cdot 2HCl$ give *N*-methylalloxazine, identical with the analogous condensation product obtained by oxidation of theobromine and with the alloxazine obtained from (II). Degradation of hydrogenated (I) yields uramil derivatives. Oxidation of (I) with alkaline $KMnO_4$ gives a substance, $C_6H_7ON_5$, m.p. 220°. Efforts to isomerise (I) to *N*-methylxanthine failed. J. N. A.

Specificity of lactoflavin. Significance of the position of the methyl groups. R. KUHN, P. DESNUELLE, and F. WEYGAND (Ber., 1937, 70, [B], 1293—1301).—Displacement of Me from the 6- to the 5- or from the 7- to the 8-position annihilates the co-enzyme action of lactoflavin and the compounds thus obtained have no growth-promoting activity. Oxidation of 5-nitro-4-amino-*m*-xylene (I) by HSO_4 affords 5-nitro-4-nitroso-*m*-xylene, m.p. 134° (decomp.), oxidised to 4:5-dinitro-*m*-xylene (II), m.p. 130°, which with NH_3 -EtOH at 165° yields only (I). Treatment of (II) with *l*-arabinamine in 80% EtOH at 135° gives 5-nitro-4-*l*-arabitylamino-*m*-xylene, m.p. 141°, reduced (Pt in 80% EtOH) and then condensed with alloxan monohydrate (III) and H_3BO_3 in presence of AcOH to 6:8-dimethyl-9-*l*-araboflavin, m.p. 256° (decomp.), $[\alpha]_D^{25} -212^\circ$ to -126° (dependent on c) in 0.2*N*-NaOH, $[\alpha]_D^{25} +165^\circ$ in 0.1*N*-NaOH + $Na_2B_4O_7$. *d*-Ribamine similarly yields 5-nitro-4-*d*-ribitylamino-*m*-xylene, whence 6:8-dimethyl-9-*d*-riboflavin, m.p. 230° (decomp.), $[\alpha]_D^{25} -275^\circ$ to -189° in 0.2*N*-NaOH (dependent on c), $[\alpha]_D^{25} +145^\circ$ in 0.1*N*-NaOH + $Na_2B_4O_7$. *l*-Arabinose, 4-nitro-5-amino-*m*-xylene, and NH_4Cl in boiling abs. EtOH afford *l*-arabinose-2-nitro-3:5-dimethylanilide, m.p. 171°, $[\alpha]_D^{25} -81.5^\circ$ in 80% EtOH (triacetate, m.p. 163°), reduced (Pd- $CaCO_3$ - Na_3BO_3 -75% EtOH) and then condensed with (III) to 5:7-dimethyl-9-*l*-araboflavin, m.p. 277° (decomp.), $[\alpha]_D^{25} -176^\circ$ to -93° (dependent on c) in 0.2*N*-NaOH, $[\alpha]_D^{25} +407^\circ$ in 0.1*N*-NaOH + $Na_2B_4O_7$. *d*-Ribose-2-nitro-3:5-dimethylanilide, m.p. 142°, gives 5:7-dimethyl-9-*d*-riboflavin, m.p. 246° (decomp.), $[\alpha]_D^{25} -47.4^\circ$ in 0.2*N*-NaOH, $+219^\circ$ in 0.1*N*-NaOH + $Na_2B_4O_7$. *p*-Methoxybenzylidene-*d*-ribamine, m.p. 137—138°, *p*-methoxybenzylidene-*l*-rhamnamine, m.p. 141—142°, and *l*-rhamnamine oxalate, m.p. 167—168°, are incidentally described. H. W.

Specificity of lactoflavin. Replacement of the methyl groups by the tetramethylene and trimethylene ring. R. KUHN, H. VETTER, and H. W. RZEPFA (Ber., 1937, 70, [B], 1302—1314).—The ability to form a catalytically active compound with proteins is retained when the $Me_{(6)}$ and $Me_{(7)}$ groups of flavins are replaced by the tri- or tetramethylene ring. 2-Nitro-3-amino-5:6:7:8-tetrahydronaphthalene (I) is converted by *p*- $C_6H_4Me \cdot SO_2Cl$ in C_5H_5N at 100° into 2-nitro-3-*p*-toluenesulphonamido-5:6:7:8-tetrahydronaphthalene, m.p. 145.5—146.5°, which with 50% KOH and Me_2SO_4 at 50° affords 2-nitro-3-*p*-toluenesulphonmethylamido-5:6:7:8-tetra-

hydronaphthalene, m.p. 198°, hydrolysed by AcOH—conc. H_2SO_4 at 100° to 2-nitro-3-methylamino-5:6:7:8-tetrahydronaphthalene, m.p. 115.5°. The last-named substance is reduced by $SnCl_2$ and conc. HCl to 2-amino-3-methylamino-5:6:7:8-tetrahydronaphthalene, m.p. 83°, the dihydrochloride, m.p. 184—186° (decomp.) when rapidly heated, of which is condensed with alloxan tetrahydrate to 6:7-tetramethylene-9-methylisalloxazine, m.p. $>360^\circ$ after decomp. at 345°. Similarly (I) is reduced to 2:3-diamino-5:6:7:8-tetrahydronaphthalene, m.p. 134.5°; the dihydrochloride, m.p. 302° (decomp.) when rapidly heated, yields 6:7-tetramethylenealloxazine, m.p. $>360^\circ$. *l*-Arabinose, (I), and NH_4Cl in boiling abs. EtOH afford 2-nitro-3-amino-5:6:7:8-tetrahydronaphthalene-*N*-*l*-arabinoside (triacetate, m.p. 217°, $[\alpha]_D^{25} +108.6^\circ \pm 1.5$ in MeOAc), reduced (Pd- $NaBO_2 \cdot H_2O$ -EtOH), condensed with alloxan and H_3BO_3 , and then acetylated to 6:7-tetramethylene-9-*l*-araboflavin tetra-acetate, m.p. 243° (decomp.). *l*-Arabinamine and 2:3-dinitro-5:6:7:8-tetrahydronaphthalene in boiling C_5H_5N give 2-nitro-3-*l*-*l*-arabitylamino-5:6:7:8-tetrahydronaphthalene, m.p. 208—209°, reduced (PtO₂ in 80% EtOH) and then condensed to 6:7-tetramethylene-9-*l*-araboflavin, m.p. 285—286°, $[\alpha]_D^{25} -45.8^\circ \pm 3^\circ$ in 0.1*N*-NaOH, $+320^\circ \pm 10^\circ$ in NaOH + $Na_2B_4O_7$. *l*-Arabinose, NH_4Cl , and 6-nitro-5-aminohydrindene in boiling abs. EtOH afford 6-nitro-5-aminohydrindene-*N*-*l*-arabinoside (triacetate, m.p. 220—220.5°), reduced and condensed to 6:7-trimethylene-9-*l*-araboflavin, m.p. 300° (decomp.), $[\alpha]_D^{25} -61^\circ \pm 4^\circ$ in 0.1*N*-NaOH, $+326^\circ \pm 10^\circ$ in NaOH + $Na_2B_4O_7$ [tetra-acetate, m.p. 200.5—201.5° (decomp.)]. 2-Nitro-3-*d*-*l*-ribitylamino-5:6:7:8-tetrahydronaphthalene has m.p. 138—139°. *d*-Ribose and 3-nitro-*p*-toluidine in boiling EtOH give 3-nitro-*p*-toluidine-*N*-*d*-ribose, reduced and condensed to 6-methyl-9-*d*-riboflavin, m.p. 276—277° (decomp.), $[\alpha]_D^{25} -62.5^\circ \pm 4^\circ$ in 0.1*N*-NaOH, $+275^\circ \pm 10^\circ$ in NaOH + $Na_2B_4O_7$. 6-Methyl-9-*l*-araboflavin, obtained similarly, has m.p. 276° (decomp.) when rapidly heated, $[\alpha]_D^{25} -67.5^\circ \pm 4^\circ$ in 0.1*N*-NaOH, $+277^\circ \pm 10^\circ$ in NaOH + $Na_2B_4O_7$. 6(7)-Methylalloxazine, decomp. 335°, is described. H. W.

Phthalocyanines. IX. Derivatives of thiophen, thionaphthen, pyridine, and pyrazine. Nomenclature. R. P. LINSTAD, E. G. NOBLE, and J. M. WRIGHT. X. Experiments in the pyrrole, isooxazole, pyridazine, furan, and triazole series. J. A. BILTON and R. P. LINSTAD. XI. Preparation of octaphenylporphyrines from diphenylmaleinitrile. A. H. COOK and R. P. LINSTAD. XII. Experiments on the preparation of tetrabenzoporphyrins. R. P. LINSTAD and E. G. NOBLE (J.C.S., 1937, 911—921, 922—929, 929—933, 933—936).—IX. Theoretical considerations of the ease of formation of the porphyrine structure in different heterocyclic systems are discussed. Coloured substances closely resembling phthalocyanines have been obtained in the thiophen (2:3), thionaphthen, C_5H_5N , and pyrazine series. Acetylation of 3-methylthiophen gives a mixture of ketones, oxidised to thiophen-2:3- and -2:4-dicarboxylic acids, which can be separated since the 2:3-acid forms an anhydride, m.p. 140°. The diamide, m.p.

228°, from the 2:3-acid, is dehydrated to the imide, m.p. 204°, and to 2:3-dicyanothiophen, m.p. 140°, which with Cu_2Cl_2 affords *Cu tetra-2:3-thiophenoporphyrzine*. Thiophen-3:4-dicarboxylic acid could not be prepared. Thionaphthen-2:3-dicarboxylamide, m.p. 204–205°, prepared from the thionaphthen-quinone, is dehydrated to the -dicarboxylimide, m.p. 240°, 2(or 3)-cyanothiophen-3(or 2)-carboxylamide, m.p. 192–194°, or 2:3-dicyanothiophen, m.p. 148°. The dinitrile and Cu_2Cl_2 afford a *Cu tetra-2:3-thiophenoporphyrzine*, containing one Cl. Quinolinamide and $\text{AcOH}\cdot\text{Ac}_2\text{O}$ yield 2(or 3)-cyano-pyridine-3(or 2)-carboxylamide (I), m.p. 255–260°, and with Ac_2O alone, the Ac derivative of quinolin-imide, m.p. 150°, is obtained. 2:3-Dicyanopyridine, m.p. 130°, is derived by catalytic treatment of the amide and NH_3 . Mg and (I) form a metallic derivative which gives *tetra-2:3-pyridinoporphyrzine (dimethiodide)*. Diaminomaleinitrile (II) condenses with glyoxal to 2:3-dicyanopyrazine, hydrolysed to pyrazinemonocarboxylic acid (cf. Grischkevitch-Trochimovski, A., 1928, 745). Ac_2O , benzil, and phenanthra-quinone condense with (II) to give respectively 2:3-dicyano-5:6-dimethyl-, m.p. 166°, and -diphenylpyrazine, m.p. 245°, and 2:3-dicyanophenanthra-(9':10':5:6)pyrazine, m.p. 320°. 3:4-Dicyanopyrazine with Cu_2Cl_2 forms *Cu tetrapyrazinoporphyrzine tetra-, tri-, and mono-hydrate*, and with Mg yields *tetrapyrazinoporphyrzine tetrahydrate*.

X. No phthalocyanine-like pigment has been isolated in any of the five series investigated. A striking difference has been observed in the ease with which heterocyclic *o*-dicarboxylic esters could be converted into the corresponding amides: amides were readily formed from esters derived from $\text{C}_5\text{H}_5\text{N}$, pyrazine, pyridazine, and isooxazole, but not from the corresponding derivatives of pyrrole and furan. 2:5-Dimethylpyrrole-3:4-dicarboxylic ester does not react with NH_3 , nor does the 1:2-diacetylsuccinate, m.p. 113.5°. α -Bromocycanoacetone, b.p. 43°/12 mm., does not condense with $\text{CN}\cdot\text{CH}_2\cdot\text{COMe}$. Decarboxylation of 3-cyano-2:5-dimethylpyrrole-4-carboxylic acid, m.p. 288° (decomp.), prepared from the Et ester, gives 3-cyano-2:5-dimethylpyrrole, m.p. 89°. This is converted into 4-formyl-3-cyano-2:5-dimethylpyrrole, m.p. 207°, the oxime, m.p. 223°, of which with $\text{NaOAc}\cdot\text{Ac}_2\text{O}$ yields 3:4-dicyano-2:5-dimethylpyrrole, m.p. 239°. Et 5-cyano-2:3-dimethylpyrrole-4-carboxylate, m.p. 180°, prepared from 4-carbethoxy-2:3-dimethylpyrrole-5-aldoxime, is hydrolysed to the acid, m.p. 242°, which could not be converted into the corresponding $(\text{CN})_2$ -compound, nor could this substance be obtained from 5-cyano-2:3-dimethylpyrrole, m.p. 121.5°. 5-Methylisooxazole-3:4-dicarboxylamide, m.p. 216°, obtained from the Et ester, is dehydrated (P_2O_5) to 3:4-dicyano-5-methylisooxazole, m.p. 32°, which with HCl forms 4(or 3)-cyano-5-methylisooxazole-3(or 4)-carboxylamide, m.p. 225°. 3:6-Dimethylpyridazine-4:5-dicarboxylamide, m.p. 240°, from the Et ester, sublimes to the -imide, m.p. 240° (decomp.). 2:5-Dimethylfuran-3:4-dicarboxylamide with Ac_2O gives 4-cyano-2:5-dimethylfuran-3-carboxylic acid, m.p. 174°. Me 5-cyano-3-methylfuran-4-carboxylate, m.p. 49°, could not be converted into the amide.

XI. Diphenylmaleinitrile (III) and Mg give Mg

octaphenylporphyrzine, which with HCO_2H yields octaphenylporphyrzine diformate, hydrolysed to octaphenylporphyrzine. The Cu compound is very stable; (III) and Cu_2Cl_2 afford *Cu monochloro-octaphenylporphyrzine*. Mg octa-*p*-nitrophenylporphyrzine is obtained from the corresponding nitrile.

XII. Reduction of 4-chloro-1-methylphthalazine with metal and acid gives only methyl-dihydroisindole (IV) (hydrochloride, m.p. 170°) and not 1-methyl-*o*-isindole (cf. Gabriel *et al.*, A., 1893, i, 348; Fenton and Ingold, A., 1929, 195). Oxidation of (IV) yields no isolable products and bromination affords 1-methyl-dihydroisindole hydrobromide, m.p. 160°. *o*-Cyanocinnamic acid and Br give the dibromide, m.p. 184–186° (decomp.), debrominated (KOH) to 1-bromo-2-*o*-cyanophenylacrylic acid, m.p. 156–158°, and *o*-cyanophenylpropionic acid, which is decarboxylated to *o*-cyanophenylacetylene, m.p. 76°. These compounds did not form stable pigments with numerous metallic reagents. *o*-Cyanocinnamitrile, m.p. 108°, is described. Although it is not possible to exclude the formation of tetrabenzoporphyrins with complete certainty, there is no pronounced tendency for their formation from the foregoing intermediates. F. R. S.

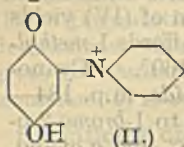
Synthesis of arylideneisooxazolones. J. J. DONLEAVY and E. E. GILBERT (J. Amer. Chem. Soc., 1937, 59, 1072–1076).—The following observations replace and amplify the erroneous conclusions of Minunni *et al.* (A., 1928, 1245; 1929, 555, 556). $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ or $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ and the appropriate aldoxime in strong acid, best 10% by wt. of 85% H_3PO_4 , give 4-benzylidene-3-methyl- (I), m.p. 146–147° (also obtained from PhCHO and $\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ in AcOH), 3-phenyl-4-benzylidene- (II), m.p. 193–194° [also obtained from phenylisooxazolone (III) and PhCHO], 3-phenyl-4-anisylidene- (IV), m.p. 164–165° [also obtained from (III) and $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$], 3-methyl-4-isopropylidene-, m.p. 120–121° (also obtained from $\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and COMe_2), and 4-anisylidene-3-methyl-isooxazol-5-one, m.p. 180–181°. Reaction occurs by hydrolysis of the oxime, condensation of the liberated aldehyde with the acylacetic ester, oximation of the product, and finally ring-closure. Aliphatic aldoximes give only resins, doubtless formed by polymerisation of the liberated aldehyde by the acid condensing medium. Na_2CO_3 at 70° decomposes (I) into PhCHO (0.5 mol.) and (?) 4:4'-benzylidenebis-3-methylisooxazol-5-one (V), m.p. 150–151° (*Et*₂ derivative, m.p. 159–161°, obtained by $\text{Et}_2\text{SO}_4\cdot\text{Na}_2\text{CO}_3$), also prepared from (I) by $\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ in AcOH at room temp. Na_2CO_3 merely hydrolyses (II) to PhCHO and (III), and it does not affect (IV). $\text{NHPh}\cdot\text{NH}_2$ in warm MeOH hydrolyses (II) and (IV), yielding the $\text{NHPh}\cdot\text{NH}_2$ salt, m.p. 153–154°, of (III); with (I) it gives $\text{CHPh}\cdot\text{N}\cdot\text{NHPh}$ and (V). The so-called 3-methylisooxazol-5-one, m.p. 168–169°, obtained from $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and NH_2OH , is 3-methyl-5-4'-3'-methylisooxazolidenisooxazole,

$$\begin{array}{c} \text{CMe}\cdot\text{CH} \\ \text{NH}-\text{O} \end{array} > \text{C} < \begin{array}{c} \text{CMe}\cdot\text{N} \\ \text{CO}-\text{O} \end{array}$$
M.p. are corr. R. S. C.

Polymerisation processes caused by pyridine.

I. O. DIELS and R. KASSEBART (Annalen, 1937,

530, 51—67).— C_5H_5N , benzoquinone (I), and the appropriate acid give C_5H_5N 2:5-dihydroxyphenylformate, m.p. 187—188° (decomp.), -acetate, m.p. 215° (decomp.), -chloride, m.p. 225° (Ac_2 derivative, + H_2O , m.p. 122°), and -maleate, m.p. 189° (decomp.), which with cold, saturated, aq. Na_2CO_3 give the enolbetaine (II), + $2H_2O$ and anhyd., m.p. 240° (decomp.); this regenerates the above salts with the appropriate acid and with $(;C\cdot CO_2H)_2$ in MeCN gives the salt, $C_{15}H_{11}O_6N$, which at the m.p., 141—142°, gives CO_2 and the propiolate, m.p. 165° (decomp.). C_5H_5N dissolves (I) with absorption of heat, giving a solution from which (II) can be isolated; addition of a few drops of HCO_2H or H_2O



causes evolution of heat and formation of a red oily product (also obtained as yellow crystals), which is considered to be $OH\cdot C_6H_3\langle \begin{smallmatrix} O & C\cdot CO\cdot C\cdot NPh \\ NPh\cdot C\cdot CO\cdot C & O \end{smallmatrix} \rangle C_6H_3\cdot OH$ (III), formed by addition of 2 mols. of (II) to 1 mol. of (I). With hot or cold MeOH (III) gives 2:5-dimethoxybenzoquinone, new m.p. 303° (decomp.), the structure of which is proved by (a) conversion by $HNO_3\text{--}H_2SO_4$ into 3:6-dinitro-2:5-dimethoxybenzoquinone (nitroanilic acid), + $6H_2O$, m.p. 86—88° with loss of H_2O , resolidifies, explodes mildly at about 170°, (b) hydrolysis (KOH) to 2:5-dihydroxybenzoquinone, m.p. 215—220° (decomp.) (Ac_2 derivative, m.p. 152—153°), and (c) bromination in hot $CHCl_3$ to the 3:6- Br_2 -derivative, m.p. 158°, which with $HBr\text{--}AcOH$ is partly reduced to 3:6-dibromo-2:5-dimethoxyquinol, m.p. 208—211° (Ac_2 derivative, m.p. 191°), and partly hydrolysed to 3:6-dibromo-2:5-dihydroxybenzoquinone, m.p. about 285° (decomp.) (Ac_2 derivative, m.p. 203—205°). H_2O converts (III) into 2:5-di-p-hydroxyphenylbenzoquinone, m.p. 260—261° (decomp.), + $PhNO_2$, HCO_2H , or $AcOH$ [Ac_2 derivative, m.p. 221—222°; (NO_2)₂-derivative, m.p. about 295° (decomp.) (Ac_2 derivative, m.p. 242°); oxime, m.p. 255° (decomp.)], the structure of which is proved by formation of the corresponding substituted quinol, m.p. 234° (Ac_4 derivative, m.p. 165—168°), and by conversion by $Me_3SO_4\text{--}KOH$ into p- $C_6H_4(OMe)_2$ and 2:5-dihydroxybenzoquinone. R. S. C.

Substituted phenyl- and benzyl-thiazolium salts. KARIMULLAH (J.C.S., 1937, 961—962).—Thioformylmonoacetyl-o-phenylenediamine and $CH_2Cl\cdot COMe$ give N-o-acetamidophenyl-4-methylthiazolium chloride, m.p. 222°, which with NaOH forms the hydrochloride, m.p. 188°, of the tert. base; N-o-tolyl-4-methylthiazolium iodide, m.p. 230° (decomp.), is similarly prepared. Condensation of 4-methylthiazole with CH_2PhCl , o- $NO_2\cdot C_6H_4\cdot CH_2Cl$, and o- $C_6H_4Cl\cdot CH_2Cl$ yields respectively N-benzyl-, m.p. 188°, N-o-nitrobenzyl-, m.p. 200°, and N-o-chlorobenzyl-4-methylthiazolium chloride, m.p. 190° (decomp.), whilst o- $C_6H_4Cl\cdot CH_2Cl$ with 2-amino-4-methylthiazole and 2-aminothiazole affords 2-o-chlorobenzylamino-4-methylthiazole hydrochloride, m.p. 260° (decomp.), and -thiazole hydrochloride, m.p. 245°. Reduction (HI-P) of the NO_2 -compound gives N-o-aminobenzyl-4-methylthiazolium chloride hydrochloride, m.p. 213° (decomp.), which is obtained through the iodide, m.p.

237° (decomp.), and with $K_3Fe(CN)_6$ did not give a cryst. substance like thiochrome. F. R. S.

Oryzanin, "antineuritic vitamin-B." VI. Constitution of oryzanin. S. OHDAKE and T. YAMAGISHI (J. Agric. Chem. Soc. Japan, 1937, 13, 1—3; cf. A., 1935, 1175, 1428).—The constitution of oryzanin (I) as 3-(6'-amino-2'-methyl-5'-pyrimidylmethyl)-4-methyl-5-β-hydroxyethylthiazole is confirmed. The dihydrochloride with Na_2SO_3 gives 6-amino-2-methyl-5-pyrimidylmethylsulphonic acid (II), m.p. >360°, and 4-methyl-5-hydroxyethylthiazole (III) (hydrochloride, m.p. 95—96°; picrate, m.p. 164°; picrolonate, m.p. 185°; platinichloride, m.p. 173°; aurichloride, m.p. 138°). With conc. HCl at 150° (I) gives 3-(6'-hydroxy-2'-methyl-5'-pyrimidylmethyl)-4-methyl-5-β-chloroethylthiazolium chloride (hydrochloride, m.p. 130°; picrolonate, m.p. 118°), whilst (II) and (III) with the same reagent give 6-hydroxy-2-methyl-5-pyrimidylmethylsulphonic acid m.p. >360°, and 4-methyl-5-β-chloroethylthiazole (hydrochloride; picrate, m.p. 139°), respectively. $KMnO_4$ oxidation of (I) yields 6-amino-2-methyl-5-aminoethylpyrimidine (hydrochloride, m.p. 263°; picrate, m.p. 225°; picrolonate, m.p. 250°; platinichloride, m.p. >290°). J. N. A.

Crystalline vitamin-B₁. XVII. Synthesis of vitamin-B₁. J. K. CLINE, R. R. WILLIAMS, and J. FINKELSTEIN (J. Amer. Chem. Soc., 1937, 59, 1052—1054; cf. A., 1937, III, 153).— $OEt\cdot C_6H_4\cdot CO_2Et$, HCO_2Et , and Na give Et sodioformyl-β-ethoxypropionate, which with $NH_4CMe\cdot NH_2\cdot HCl$ and NaOEt gives 6-hydroxy-2-methyl-5-ethoxymethylpyrimidine, m.p. 175—176° (3.5% yield), and thence by $POCl_3$ at 78° the 6-chloro-, b.p. 72—73°/0.5 mm., and by $NH_3\text{--}EtOH$ at 140° the substituted 6-amino-pyrimidine, m.p. 89.5—90.5°, the hydrobromide, m.p. 192—193°, of which with 4-methyl-5-β-hydroxyethylthiazole in BuOH at 120° gives 45% of vitamin-B₁ bromide hydrobromide, forms, m.p. 232—234° and 248—250°. The vitamin salts under crossed Nicols appear to undergo change at 190° and the m.p. are not sharp or characteristic. The forms do not differ crystallographically, spectrometrically, electrometrically, or pharmacologically. R. S. C.

Azacyanines. (Miss) N. I. FISHER and (Miss) F. M. HAMER (J.C.S., 1937, 907—911).—2-Iodoquinoline ethiodide and 2-aminopyridine give 2:2'-pyridylaminoquinoline ethiodide, m.p. 216° (methiodide, m.p. 206°), which, after removal of HI, with EtI affords 1:1'-diethyl-2-pyrido-2'-azacyanine iodide or (1-ethyl-2-pyridine)(1-ethyl-2-quinoline)azamethincyanine iodide, m.p. 240°. Similarly prepared are 1-methyl-1'-ethyl-, m.p. 232°, and 1:1'-dimethyl-2-pyrido-2'-azacyanine iodide, m.p. 258°, 1:2'-diethyl-2-pyrido-1'-azacyanine iodide, m.p. 213°, and 3:1'-diethylthiazolo-2'-azacyanine iodide, m.p. 239°. Condensation of 2-ethylbenzthiazolonehydrazine with the p-dimethylaminoanil of quinaldehyde ethobromide, of benzthiazole-1-aldehyde ethochloride, and of benzselenazole-1-aldehyde ethobromide [+0.5MeOH, m.p. 225° (decomp.)] yields respectively 2:1'-diethyl-αβ-diazathia-2'-carbocyanine bromide or (1-ethyl-2-quinoline)(2-ethyl-1-benzthiazole)-αβ-diazatrimethincyanine bromide, m.p. 221° (decomp.), 2:2'-diethyl-αβ-

diazathiacarbocyanine bromide or bis-(2-ethyl-1-benzthiazole)- $\alpha\beta$ -diazatrimethincyanine bromide, m.p. 219° (decomp.), and 2:2'-diethyl- $\beta\gamma$ -diazaselenathiacarbocyanine bromide or (2-ethyl-1-benzthiazole)(2-ethyl-1-benzselenazole)- $\alpha\beta$ -diazatrimethincyanine bromide, m.p. 259° (decomp.). 1-Methylbenzthiazole ethiodide, NaOAc, Ac₂O, and 1- β -acetanilidovinylbenzthiazole and -selenazole give respectively 2:1'-diethylthia-2'-carbocyanine iodide, m.p. 248° (decomp.) (Ogata, A., 1934, 1370), and 2:2'-diethylselenathiacarbocyanine iodide or (2-ethyl-1-benzthiazole)(2-ethyl-1-benzselenazole)trimethincyanine iodide, m.p. 257° (decomp.). 2-Aminoquinoline ethiodide, Et orthoformate, and C₅H₅N form 1:1'-diethyl- $\alpha\gamma$ -diaz-2:2'-carbocyanine iodide or bis-(1-ethyl-2-quinoline)- $\alpha\gamma$ -diazatrimethincyanine iodide, m.p. 209° (1:1'-dimethyl compound, m.p. 193°). Absorption and sensitising data are recorded.

F. R. S.

Constitution of nymphaëine. E. BUREŠ and F. PLZÁK, jun. (Časopis českoslov. Lék., 1935, 15, 223—226, 242—247; Chem. Zentr., 1936, i, 3340).—An improved method of isolation from roots of *Nymphaea alba* is described. The crude alkaloid is amorphous, m.p. 76—77°, but forms a cryst. hydrochloride, m.p. 230°, and sulphate; the regenerated nymphaëine has m.p. 71—72°, is a sec. base, C₁₄H₂₃O₂N, and has a pyrrole nucleus and 1 OH.

H. N. R.

Properties of the ecgonines and their esters. III. $\alpha\beta$ -Position of the double linking in ecgonidine; the structural formulæ and autoracemisation of the ecgonines. A. W. K. DE JONG (Rec. trav. chim., 1937, 56, 678—680).—The presence of a double linking at $\alpha\beta$ in ecgonidine has already been established by Willstätter, Gadamer, and von Auwers. *l*-Ecgonine is partly racemised when heated with H₂O.

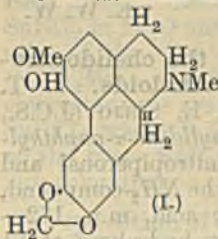
H. W.

Lupin alkaloids. XII. Synthesis of *dl*-lupinine and *dl*-isolupinine. G. R. CLEMO, W. MCG. MORGAN, and R. RAPER (J.C.S., 1937, 965—969).—Several methods of approach for a satisfactory lupinine synthesis have been investigated, one of which has given *dl*- and *dl*-iso-lupinine in amounts too small for resolution. Me 1-keto-octahydropyridocoline-9-carboxylate and N₂H₄ give in small yield 3-ketodecahydropyridopyridocoline, m.p. 137°. Bromination of 2-acetylpyridine affords ω -bromoacetylpyridine, b.p. 88°/1 mm., in which the Br could not be replaced by OMe or OPh. Et 2-pyridylacetate (I), HCO₂Et, and K form *Et* hydroxymethylene-2-pyridylacetate (II), m.p. 97°, which could not be readily reduced, and which with Al(OPrⁱ)₃ and PrⁱOH gives Prⁱ hydroxymethylene-2-pyridylacetate, m.p. 78° (picrolonate of Prⁱ 2-pyridylacetate, m.p. 187°). Catalytic hydrogenation of (II) yields a mixture of picrolonates: of Et pyridyl- α -propionate (?), m.p. 124°, *C*, m.p. 209°, and *D*, m.p. 185°. Condensation of the base from *C* with CH₂Cl·CH₂·CO₂Et gives *Et* piperidyl-1- β -propionate-2- α -propionate *E*, b.p. 136—138°/1 mm. (picrolonate, m.p. 115°), and similarly the base from *D* affords an isomeric ester *F*, b.p. 145°/1 mm. (picrolonate, m.p. 136°). Reduction (K-PhMe) of *E* and *F* leads to 2-keto-1-methyloctahydropyridocoline, b.p. 78—80°/1 mm. (picrate, m.p. 202°; picrolonate, m.p. 209°). Condensation of (I) and CH₂Cl·CO₂Et

gives *Et* pyridylsuccinate, b.p. 143—147°/1 mm. (picrolonate, m.p. 95°), which is reduced (PtO₂-H₂) to *Et* 2-piperidylsuccinate (?) (picrolonate, m.p. 166°), further cyclised to *Et* 3-keto-octahydropyridocoline-1-carboxylate, b.p. 148—150°/1 mm. γ -Phenoxy-*n*-propyl bromide and (I) condense to *Et* 8-phenoxy- α -2-pyridyl-*n*-valerate, b.p. 205—207°/1 mm., reduced catalytically to the -piperidyl ester, b.p. 190—192°/1 mm., which is further reduced (Na-EtOH) to ϵ -phenoxy- β -2-piperidyl-*n*-amyl alcohol, b.p. 195—200°/1 mm. The carbinol with HBr followed by PBr₃ gives a mixture of *dl*-bromolupinane *L*, b.p. 107°/1 mm. (picrolonate, m.p. 202°; methiodide, m.p. 216°; picrate, m.p. 135°), and *M*, b.p. 107°/1 mm. (picrolonate, m.p. 169°; picrate, m.p. 144°). Hydrolysis (NaOAc) of *L* affords 1-octahydropyridocolyl-carbinol *N*, b.p. 107°/1 mm., m.p. 59° [methiodide, m.p. 303° (decomp.); picrolonate, m.p. 203°; picrate, m.p. 127°], and of *M* yields the carbinol *O*, b.p. 122°/1 mm., m.p. 81° (picrate, m.p. 139°; picrolonate, m.p. 225°; methiodide, m.p. 248°). The compounds *N* and *O* should be either *dl*- or *dl*-iso-lupinine.

F. R. S.

Constitution of domesticine. Z. KITASATO and



H. SHISHIDO (Acta phytochim., 1937, 9, 265—266).—6-Methoxy-7-ethoxy-1-6'-aminopiperonyl-2-methyltetrahydroisoquinoline is converted into 6'-methoxy-5-ethoxy-2:3-methylenedioxy-*N*-methylaporphine, the *d*-form of which, m.p. 131°, [α]_D +110°, is identical with domesticine Et ether.

Domesticine is therefore (I).

H. W.

Strychnine and brucine. XXXVI. Preliminary synthetic experiments. H. I. OPENSCHAW and R. ROBINSON (J.C.S., 1937, 941—946).—cycloHexanone-2- β -propionic acid condenses with NHPh·NH₂ to give the lactam of tetrahydrocarbazole-1- β -propionic acid, m.p. 126°, and tetrahydrocarbazolenine-11- β -propionic acid (I), m.p. 226°. The lactam is reduced electrolytically to 1:9-trimethylenhexahydrocarbazole, m.p. 81—82°, dehydrogenated to 1:9-trimethylene-1:2:3:4-tetrahydrocarbazole, m.p. 86—87°. (I) is reduced (Sn-HCl) and acetylated to *N*-acetylhexahydrocarbazole-11- β -propionic acid, m.p. 202°. Et 2-carbethoxycyclohexanone-2- β -propionate and NaOEt give *Et* 6-carbethoxycyclohexanone-2- β -propionate, b.p. 189—190°/11 mm., which with CH₂Cl·CH₂·CO₂Et in C₆H₆ affords the -2:6- $\beta\beta'$ -dipropionate (II), b.p. 182—183°/0.2 mm., and in EtOH yields some *Et* heptane-1:3:7-tricarboxylate, b.p. 147—148°/0.15 mm. (II) is hydrolysed (HCl) to cyclohexanone-2:6- $\beta\beta'$ -dipropionic acid, m.p. 145°. The phenylhydrazone of the Et ester, m.p. 60—61°, of this acid, with EtOH-HCl, followed by reduction gives the lactam, m.p. 271°, of hexahydrocarbazole-1:11- $\beta\beta'$ -dipropionic acid. A reply is made to the criticisms of Kotake (cf. A., 1936, 1003).

F. R. S.

Veratrine alkaloids. I. Degradation of cevine. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1937, 119, 141—153).—Cevine heated in H₂ with soda-lime gives, first H₂O, then an unsaturated oily distillate catalytically reduced to a complex mixture,

giving first a neutral fraction (I), then a fraction (II), b.p. 60—70°/8 mm., and a fraction, b.p. 100—140°/8 mm. The distillate also contains [*l*?]-coniine (cf. J.C.S., 1922, 121, 1571); *d*-coniine forms a 2 : 4-dinitrobenzoyl derivative, m.p. 108°. From (II), a picrate (III), m.p. 148—150°, and an unsaturated picrate, m.p. 118—120°, hydrogenated to (III), are obtained. After decomp. by HCl, (III) gives a mixed methiodide, m.p. 200—230°, which with Ag₂O-MeOH, followed by distillation and catalytic reduction, gives a base, C₁₁H₂₃N (picrate, m.p. 138—140°), of which the methiodide, m.p. 248—250°, is converted by Ag₂O etc. into a base, C₁₂H₂₅N [hydrochloride, m.p. 185—193° (subliming)]; *platinichloride*, m.p. 118—120°, resembling, but not identical with, dimethyl-*n*-decylamine. Fractionation of (I) gives an oil, C₇H₁₂O (semicarbazone, m.p. 217—219°), an oil, b.p. 150—160°/25 mm., a hydrocarbon, b.p. 120—130°/0.2 mm., and an oil, C₁₁H₁₈O (semicarbazone, m.p. 160—170°). Covine heated in H₂ with Zn dust gives a product catalytically hydrogenated to bases, C₇H₁₅N, apparently active *N*-methyl-β-pipecoline (picrate, m.p. 178—180°), C₈H₁₁N (picrate, m.p. 128—133°), and C₉H₁₃N (picrate, m.p. 131—142°). E. W. W.

Synthetical experiments in the chelidonine-sanguinarine group of the alkaloids. I. T. RICHARDSON, R. ROBINSON, and E. SELJO (J.C.S., 1937, 835—841).—6-Nitropiperonylidene- α -naphthylamine, m.p. 151—153°, from 6-nitropiperonal and α -C₁₀H₇-NH₂, is reduced (Na₂S) to the NH₂-compound, m.p. 150—151°. Veratrysuccinic acid, m.p. 172—174° (+H₂O, m.p. 126—128°), by hydrolysis of Et α -cyano-β-veratrylacrylate, gives the Me ester, m.p. 64—66°, which with piperonal affords the anhydride, m.p. 127—129°, of piperonylideneveratrysuccinic acid. These substances could not be used as starting points of the desired reactions. Veratraldehyde and acetoveratrone form 3 : 4 : 3' : 4'-tetramethoxychalkone (I), m.p. 116—118°, which with NH₂OH leads to a substance, m.p. 152—154°, with NHPH-NH₂·HCl yields the phenylhydrazone or pyrazoline, m.p. 159—160°, and is reduced to α -keto- α -diveratrylpropane, m.p. 88—90°. (I) and NaCN in MeOH give γ -keto- α -cyano- α -diveratrylpropane, m.p. 143—144°, hydrolysed to β-veratroyl- α -veratrylpropionamide, m.p. 160—162°, which affords the propionic acid, m.p. 193—194° [phenylhydrazone anhydride (?), m.p. 149—151°]. This acid is reduced (Zn-Hg) to α -diveratrylbutyric acid, m.p. 118—120° [(NO₂)₂-derivative, m.p. 186—188°], which is cyclised (POCl₃) to 1-keto-6 : 7-dimethoxy-2-veratryl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 147—149°, from the oxime, m.p. 200—202°, of which the 1-NH₂-compound, m.p. 119—121°, is obtained by reduction (Na). This amine gives a formamido-derivative, m.p. 202—203°, which is dehydrated (POCl₃) to 6 : 7 : 4' : 5'-tetramethoxy-3 : 4 : 11 : 12-tetrahydro-1 : 2-benzphenanthridine, m.p. 230—231°.

Veratraldehyde and acetopiperone condense to veratrylideneacetopiperone, m.p. 133—135°, which with HCN forms γ -keto- α -cyano- α -veratryl- γ -piperonylpropane, m.p. 144—146°, converted into α -veratryl-β-piperonylpropionamide, m.p. 178—180°. Piperonylacetone and Na yield 6-amino-5-piperonyl-2 : 4-

dihomopiperonylpyrimidine, m.p. 170—171°, and chiefly β-imino- α -cyano- α -diveratrylpropane, m.p. 113—114°, converted into the β-keto-compound, m.p. 122—123° (oxime, m.p. 150—151°). The imino-compound and keto-nitrile could not be converted into C₁₀H₈ derivatives by the action of HCl-AcOH. Veratrylacetonitrile (II) and Na give β-imino- α -cyano- α -diveratrylpropane, m.p. 132—133°, and a trimeride, m.p. 168—168.5. 6-Bromoveratrylacetonitrile, m.p. 90—92°, from (II) and Br, could not be dimerised. F. R. S.

Sterin alkaloids. H. ROCHELMEYER (Arch. Pharm., 1937, 275, 336—342).—Glucosido-alkaloids containing the methylcyclopentenophenanthrene (I) nucleus are termed sterin alkaloids. Solanine-*l* and -*s* are renamed solatunine and solasonine (II) and their aglucones solatubine (III) and solasodine (IV). (IV) [hydriodide, m.p. 228—229° (uncorr.)] contains 23—27 C, crystallises with 0.5H₂O or 1 mol. of dioxan, gives 1.16 mols. of AcOH, gives a 1 : 2 digitonide, and with Se affords (I) and a pyrrole derivative (crude picrate, m.p. 140—142°). With NaOH-MeOH (III) gives solanosodine, C₂₇H₄₁ON or C₂₉H₄₅ON, +0.5H₂O, m.p. 176—177°, which gives no digitonide. The absorption spectra of (II), solatubene, and (III) are detailed and formulæ are discussed. R. S. C.

Organo-arsenic compounds. III. Arsination of phenol and derivatives of hydroxyphenyl-arsinic acids. P. S. YANG and T. Y. WANG (J. Chinese Chem. Soc., 1937, 5, 89—95).—Arsination of phenol (A., 1923, i, 1149) yields *p*- and *o*-hydroxyphenyl-, *pp'*- and *op'*-dihydroxydiphenyl-, and *oo'*-dihydroxydiphenyl-arsinic acids, the last m.p. 209—210°. The Sb, Bi, and Hg salts of *p*- and *o*-hydroxyphenylarsinic acids were prepared. A. LI.

Arsenicals containing the dibenzfuran nucleus. B. F. SKILES and C. S. HAMILTON (J. Amer. Chem. Soc., 1937, 59, 1006—1008).—Arsination of dibenzfuran is shown to occur at position 3. H₃AsO₄ at 175—220° gives dibenzfuran-3-arsinic acid, m.p. >250°, converted by PCl₃ in AcOH into the 3-dichloroarsine, an oil, hydrolysed to the 3-arsine oxide, m.p. >250°; with Hg(OAc)₂ etc. this yields the 2-mercurichloride, m.p. 235°. 2-Aminodibenzfuran affords (Bart) dibenzfuran-2-arsinic acid (I), m.p. >275°, and thence the 2-dichloroarsine, m.p. 130°, and 2-arsine oxide, m.p. >250°. 6-Nitrodibenzfuran-2-arsinic acid (II), m.p. >280°, is obtained from 6-nitro-2-aminodibenzfuran by the Bart reaction and by nitration (HNO₃, *d* 1.48) at 5° of (I), and gives the dichloroarsine, m.p. 152° [which with Hg(OAc)₂ at 350° gives 3-nitrodibenzfuran], and arsine oxide, m.p. >250°. With H₂-Raney Ni (II) gives 6-amino-dibenzfuran-2-arsinic acid, m.p. >250°. H₂SO₄ and (I) at 100° yield the (? 8)-sulphonic acid, m.p. >300°, and thence (? 8)-sulphodibenzfuryl-2-arsine oxide, m.p. >275°. R. S. C.

Salts of tetrahydro-*N*-methylnicotinic acid methyl ester with amino-substituted arsinic acids.—See B., 1937, 730.

Derivatives of *o*-hydroxyphenylmercury chloride. H. P. ANDERSON and M. C. HART (J. Amer. Chem. Soc., 1937, 59, 1115—1116).—Bacteriostatic

data are recorded for *o*-hydroxyphenylmercuri-acetate, m.p. 150—151°, -nonoate, m.p. 135°, -oleate, m.p. 95—96°, -laurate, m.p. 135.5—136.5°, -myristate, m.p. 135—136°, -palmitate, m.p. 129—131°, and -stearate, m.p. 135—137°, and *o*-hydroxyphenylmercuri-succinimide (I), m.p. 232—235°, -saccharin, m.p. 242—243°, -phthalimide, m.p. 223—224°, -piperidine (hydrochloride, m.p. 126°), -theobromine, +H₂O, m.p. 145—165°, and -barbituric acid. Bactericidally (I) is as effective as *o*-OH·C₆H₄·HgCl. Compounds could not be obtained from pyrrole, auramine, or carbazole.

R. S. C.

Mercuration of *O*-trimethylgallaldehyde and related substances. I. M. SHARP (J.C.S., 1937, 852—853).—Mercuration of *O*-trimethylgallaldehyde gives 2-acetoxymercuri-3:4:5-trimethoxybenzaldehyde, m.p. 145—146°, which is sol. in oils. The following compounds are not oil-sol.: 2-bromomercuri-3:4:5-trimethoxybenzoic acid, m.p. 194° (basic salt, m.p. 190°), and chloromercuri-compound, m.p. 212° (from *O*-trimethylgallaldehyde); 2-bromomercuri-4-hydroxy-3:5-dimethoxybenzaldehyde, m.p. 260—265° (from syringaldehyde); and 2-chloromercuri-4-hydroxy-3:5-dimethoxybenzoic acid, m.p. 230° (decomp.) (from syringic acid).

F. R. S.

Mercuration of "acetone anil." P. KALNIN (Latvij. Univ. Raksti, 1936, 3, 315—320).—The condensation product of CMe₂ and NH₂Ph yields a Hg derivative containing 63.47% Hg, probably C₁₂H₁₂NHg₄(OAc)₅ (one OAc group being in a special position). This is reduced by H₃PO₃ to a base with an odour of quinoline.

A. LI.

Mercuration of nitrotoluidines. A. E. GODDARD (J.C.S., 1937, 984—986).—Mercuration (Hg acetate) of the nitrotoluidine gives the acetoxymercuri-derivative (in the 5-position), which with EtOH·AcOH forms a quinoneimide: 4-nitro-5-, m.p. 212° (quinoneimide, m.p. about 250°), and 5-nitro-3-acetoxymercuri-*o*-toluidine, m.p. 223° (quinoneimide, m.p. >300°); 6-nitro-4(?)-acetoxymercuri-*m*-toluidine, m.p. >300°; and 2-nitro-5- (quinoneimide), and 3-nitro-5(?)-acetoxymercuri-*p*-toluidine.

F. R. S.

Monoacetoxymercurialkylphenolsulphonic acids.—See B., 1937, 730.

Manufacture of water-soluble heterocyclic mercury compounds [pyridines].—See B., 1937, 730.

Interaction of selenium tetrachloride and benzene in presence of anhydrous aluminium chloride. W. E. BRADT and J. F. GREEN (J. Org. Chem., 1937, 1, 540—543).—SeCl₄ (50) and AlCl₃ (30) in C₆H₆ (136.5 g.) give PhCl (1), Ph₂Se (20), b.p. 301—303°/700 mm. (identified by conversion into SePh₂Cl₂, m.p. 183°), Ph₂Se₂ (I) (5), m.p. 63° [2HgCl₂-additive compound, m.p. 187—188° (corr.)], and SePh₃Cl, isolated as SePh₂Cl·ZnCl₂ (20 g.), m.p. 274°. The reaction is formulated: SeCl₄ + 3C₆H₆ → SePh₃Cl + 3HCl; SePh₃Cl → Ph₂Se + PhCl; Ph₂Se + Se → Ph₂Se₂. (I) with Br gives SePh₂Br₂, converted by heat into (*p*-C₆H₄Br)₂Se, m.p. 115°.

R. S. C.

1:2-Diselenacyclopentanes. H. J. BACKER and H. J. WINTER (Rec. trav. chim., 1937, 56, 691—698).

—Interaction of CPhMe(CH₂Br)₂ with K₂Se affords the hydrocarbon C₁₀H₁₂, b.p. 176°/750 mm. (also obtained by the action of Zn), and 4-phenyl-4-methyl-1:2-diselenacyclopentane (I), $\text{Se}-\text{CH}_2-\text{CH}_2-\text{Se}-\text{CPhMe}$, m.p. 114—114.5°, better obtained by use of K₂Se₂. (I) is oxidised by HNO₃ to β-phenyl-β-methylpropane-αγ-diseleninic acid, m.p. 113° (decomp.) (dinitrate, decomp. about 70°). CMe₂(CH₂Br)₂ and KCNSe in EtOH at 140° yield αγ-diselenocyclopropane-ββ-dimethylpropane (II), m.p. 69.5°, converted by NaOEt in EtOH into 4:4-dimethyl-1:2-diselenacyclopentane, m.p. 34°, which is oxidised by HNO₃ to ββ-dimethylpropane-αγ-diseleninic acid, m.p. 115° (decomp.), the dinitrate, m.p. 125—126° (decomp.), of which is also produced by the oxidation of (II). According to conditions (II) and Br afford αγ-bromoselenol-ββ-dimethylpropane, m.p. 127—128°, or α-bromoselenol-γ-tribromoselenol-ββ-dimethylpropane SeBr·CH₂·CMe₂·CH₂·SeBr₃, m.p. 114—115° (decomp.), which are inter-convertible.

H. W.

Complex formation and halochromy in organic tin compounds. K. A. KOTSCHESCHKOV (Sci. Rep. Moscow State Univ., 1934, No. 3, 297—303).—SnRCl₃ in Et₂O and C₅H₅N in Et₂O at 0° yield double salts of the type SnRCl₃·2C₅H₅N (R = Ph, *o*- and *p*-C₆H₄Me). Coloured complexes of CPh₃Cl with chlorostannans are formed only with those of the type SnRCl₃, where R is aryl, but not alkyl; compounds of the types SnR₂Cl₂, SnR₃Cl, or SnR₄ do not give any coloration.

R. T.

Preparation of tin triaryl halides. R. POHLAND (Ber., 1937, 70, [B], 1458).—The prep. of SnAr₃Hal from SnAr₄ and SnCl₄ at high temp. has been developed in principle by Grüttner (A., 1915, i, 335).

H. W.

Nature of the linkings in proteins. D. M. WRINCH (Nature, 1937, 139, 718).—A discussion and a reply to criticism.

L. S. T.

Intramolecular folding of proteins by keto-enol interchange. W. T. ASTBURY and D. M. WRINCH (Nature, 1937, 139, 798).—A keto-enol interchange can be used as an alternative mechanism to the lactam-lactim interchange recently proposed for the intramol. folding of protein mols.

L. S. T.

Formation of ammonia by boiling certain proteins with alkali. G. LAUDE (Compt. rend., 1937, 204, 1428—1431).—The variation with time of the rate of evolution of NH₃ on boiling casein, gelatin, and fibrin with KOH is recorded.

A. LI.

Constituents of hydrochloric acid hydrolysates of elastin. R. ENGELAND and W. BIEHLER (Bull. Soc. Chim. biol., 1937, 19, 100—108; cf. A., 1936, 352).—The leucine fraction of the hydrolysate yields two diamino-dicarboxylic acids, C₁₃H₂₂₍₂₄₎O₄N₂ ("hammatine"), m.p. 255—258° (decomp.), [α]_D approx. -6°, and C₁₄H₂₀O₄N₂ (isolated as Cu salt).

F. O. H.

Ultracentrifugal studies of compounds of proteins with polysaccharides.—See A., III, 252.

Sulphites as protein precipitants.—See A., III, 296.

Crystallisation of melts ("freezing-out") and centrifuging as a preparative method in organic chemistry. L. RAMBERG (*Svensk Kem. Tidskr.*, 1937, 49, 134—138).—A variable-temp. centrifuge for separation of semi-solid melts is described.

M. H. M. A.

Application of nitric acid to ashing. B. S. DMITRIEV (*J. Appl. Chem. Russ.*, 1937, 10, 917—919).—The ash obtained from incineration of org. substances with addition of HNO_3 contains $>0.01\%$ of nitrite.

R. T.

Modification of the Friedrich absorption apparatus for micro-carbon-hydrogen determination. E. ABRAHAMCZIK (*Mikrochem.*, 1937, 22, 227—232).—A modified form of absorption tube is described.

J. S. A.

Manometer for carbon and hydrogen pressure regulation. W. H. HAMILL (*Ind. Eng. Chem. [Anal.]*, 1937, 9, 355).

E. S. H.

Detection of elements in organic substances. L. ROSENTHALER (*Z. anal. Chem.*, 1937, 109, 31—35; cf. this vol., 128).—C may be detected as CO_2 by wet oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ + syrupy H_3PO_4 at 250° and H, as H_2S , by heating with Na_2SO_3 (cf. A., 1930, 1460). $\text{Na}_2\text{S}_2\text{O}_3$ is not desirable as S is thereby liberated. P may be converted into PH_3 , detected by its green flame coloration, by heating the material with Mg powder in a closed Fe crucible, and subsequently treating the product with H_2O . As and Sb may be detected by application of the Marsh-Gutzeit test to the undestroyed material.

J. S. A.

Electrically-heated, thermostatically-controlled, constant-temperature device for Pregl carbon and hydrogen determination. F. SCHNEIDER and H. L. VAN MATER (*Ind. Eng. Chem. [Anal.]*, 1937, 9, 295).

E. C. S.

Volumetric determination of oxygen in organic compounds. J. LINDNER and W. WIRTH (*Ber.*, 1937, 70, [B], 1025—1038).—The substance (about 4 mg.) is volatilised in H_2 , degraded by a glowing Ni spiral, and the products are passed over heated CaO if halogen is present. This is followed by hydrogenation over finely-divided Ni, passage over CaO , and again over Ni. The moist gas stream passes over naphthylphosphoryl chloride. The liberated HCl is collected in H_2O and titrated with $0.1N\text{-Ba(OH)}_2$. The apparatus is figured.

H. W.

Micro-analytical determination of oxygen in organic compounds. J. UNTERZAUCHER and K. BÜRGER (*Ber.*, 1937, 70, [B], 1392).—The method depends on the catalytic hydrogenation of O to H_2O in presence of Ni- ThO_2 on an inert carrier. The substance is degraded by SiO_2 at 1000° and hydrogenation is effected at 300° .

H. W.

Direct determination of oxygen in organic compounds by hydrogenation. P. GOODLOE and J. C. W. FRAZER (*Ind. Eng. Chem. [Anal.]*, 1937, 9, 223—225).—Use of an active Ni chromite catalyst at 400° makes the ter Meulen method suitable for determination of O in org. compounds containing C, H, O, N, and S. Low results are obtained with tartaric acid and sucrose.

F. N. W.

Determination of nitrogen in refractory organic substances by a modified Dumas micro-method. J. R. SPIES and T. H. HARRIS (*Ind. Eng. Chem. [Anal.]*, 1937, 9, 304—306).—After the first, incomplete, combustion of the refractory substance, the current of CO_2 is stopped and the reduced CuO reoxidised by O_2 generated by heating KClO_3 contained in a separate boat. This process is repeated until combustion is complete.

E. C. S.

Modified micro-Dumas nitrogen determination with readily available air-free carbon dioxide. F. BREUER (*Ind. Eng. Chem. [Anal.]*, 1937, 9, 354—355).—Apparatus and technique are described.

E. S. H.

Kjeldahl digestion apparatus. W. M. CLARK (*Ind. Eng. Chem. [Anal.]*, 1937, 9, 338—339).

E. S. H.

Determination of nitrogen by modified Kjeldahl methods. W. R. CAMPBELL and M. I. HANNA (*J. Biol. Chem.*, 1937, 119, 1—7).—Addition of Se to a 3:1 mixture of H_2SO_4 and H_3PO_4 containing Cu produces a rapid and effective reagent for digesting nitrogenous material.

J. N. A.

Detection of sulphur in organic compounds. Preparation of the necessary reagent. H. FREYTAG (*Z. anal. Chem.*, 1937, 109, 93—95; cf. A., 1934, 1321).—The advantages are outlined of detecting SO_2 , formed by oxidation, by means of irradiated 2-benzoylpyridine (obtained by irradiation of a 0.2% solution of the base in 50% aq. EtOH with light of $\lambda > 3000 \text{ \AA}$). The solution so prepared may be used to impregnate test-papers.

J. S. A.

Micro-determination of sulphur in organic substances. P. PIUTTI and D. DINELLI (*Gazzetta*, 1937, 67, 133—136).—The substance, in fuming HNO_3 , is electrolysed in a cylindrical vessel with the anode at the bottom, and the resulting H_2SO_4 determined as BaSO_4 . The method is successful with CS(NHPh)_2 , sulphides, sulphonic acids, etc., but gives low vals. for S in sulphonal, sulphobenzide, and dinitrothiophen.

E. W. W.

Micro-, semimicro-, and macro-determination of halogens in organic compounds. W. H. RAUSCHER (*Ind. Eng. Chem. [Anal.]*, 1937, 9, 296—299).— $\text{NH}_2\text{[CH}_2\text{]}_2\text{OH}$ is substituted for EtOH in Stepanov's method; it readily converts aliphatic halogen into the ionic form, but is without action on aromatic halogen except of the activated type. Two procedures are described, for the determination of total and aliphatic (or reactive) halogen, respectively, and a qual. test for distinguishing the two types is developed.

E. C. S.

[Determination of] arsenic [in organic matter]. C. C. CASSIL (*J. Assoc. Off. Agric. Chem.*, 1937, 20, 171—178).—Although excellent catalysts for the breakdown of refractory org. matter, CuSO_4 , HgO , and Se interfere in the subsequent Gutzeit test. HClO_4 has no such objection and a procedure is outlined employing this agent. Dry ashing with $\text{Ce(NO}_3\text{)}_3$ and $\text{Mg(NO}_3\text{)}_2$ gave 14—17% and 100% recoveries of As, respectively, from shrimp and tobacco. The most satisfactory stains were produced by 20-mesh spherical granular Zn. A method of impregnating strips with HgBr_2

is described which produces curves of standard slope and curvature. E. C. S.

Micro-elementary analysis of organic boron compounds. H. ROTH (Angew. Chem., 1937, 50, 593—595).—For C and H combustions, org. B compounds are mixed with V_2O_5 as an oxidation catalyst, to prevent the formation of B carbides. V_2O_5 has advantages over $K_2Cr_2O_7$ for other combustions also. B is determined volumetrically by titration of H_3BO_3 in presence of mannitol. The compound is first fused with Na_2CO_3 , or, where possible, B is distilled off as $B(OMe)_3$ by heating with $H_2SO_4 + MeOH$; a suitable form of apparatus is described. Metals are determined as sulphates by evaporating the compounds down with $H_2SO_4 + MeOH$. J. S. A.

Determination of organic phosphorus by the Parr bomb method. C. L. TSENG and F. WEI (Sci. Rep. Nat. Univ. Peking, 1937, 2, 15—16).—The sample is fused with Na_2O_2 in a Parr S bomb, the product dissolved in H_2O , a slight excess of 6*N*- HNO_3 added, and the solution evaporated to <100 c.c. After filtration the vol. is adjusted to about 100 c.c., and a mixture of 6*N*- HNO_3 (30 c.c.), H_2O (20 c.c.), and Noyes' NH_4 molybdate solution (50 c.c.) is added. After warming at 60—65° for 1 hr. the yellow ppt. is filtered on a Gooch crucible, washed with 5% aq. NH_4NO_3 containing 1% HNO_3 until the washings are free from Mo, dried at 160°, and weighed. J. W. S.

Application of chromous salts to reductometric determination of organic substances. A. P. TERENTIEV and G. S. GORIATSCHEVA (Sci. Rep. Moscow State Univ., 1934, No. 3, 277—282).—The prep. of standard $CrCl_2$ solutions, and their use for titration of quinones and azo- and NO_2 -compounds, are described. R. T.

Micro-analysis for exchangeable hydrogen. W. H. HAMILL (J. Amer. Chem. Soc., 1937, 59, 1152—1153).—A technique, depending on the decrease in d of D_2O , is described for determining exchangeable H with 2—5 mg. of a H_2O -sol., non-volatile substance. The following nos. of exchangeable H are found, the second val. (if given) being due to slow exchange: $CO(NH_2)_2$ 4, glycine 3.13, histidine hydrochloride 6.07, 6.36, natural and synthetic vitamin-B₁ hydrochloride 3.6—3.94, 4.5—4.83, quinol 1.95, HCO_2Na 0, succinic acid 2.14, $CH_2(CO_2H)_2$ 2, 3.99. R. S. C.

Determination of unsaturated hydrocarbons in mixtures. Thiocyanogen iodide in volumetric analysis. H. P. KAUFMANN and H. GROSSE-OETRINGHAUS (Ber., 1937, 70, [B], 911—915).—A mixture of pure C_6H_6 , Ac_2O , and $AcOH$ is kept for at least 8 days, after which $Pb(CNS)_2$ and Br are added and the mixture is shaken in diffused light until decolorisation is complete. After addition of I the mixture is filtered; the filtrate retains a const. titre for months in the dark. A weighed quantity of mineral oil is kept with excess of this CNSI solution for 24 hr. in the dark, after which aq. KI is added and the liberated I is immediately titrated with $Na_2S_2O_3$. A blank experiment is advisable. Only in exceptional cases is the harmony of CNS and CNSI vals. satisfactory. The former are generally the higher and

do not show a pronounced termination either owing to continued addition of CNS or, more important, to ready reaction with other components of the technical materials examined. A well-marked termination of the addition of CNSI is observed. CNS appears better adapted to the examination of oils and fatty acids than is CNSI since addition of the latter is not sufficiently selective, and although pauses in the addition to substances with several unsaturated linkings exist, they are easily passed. H. W.

Semimicro qualitative test for the nitro-group in organic compounds. W. M. HEARON and R. G. GUSTAVSON (Ind. Eng. Chem. [Anal.], 1937, 9, 352—353).—45 NO_2 -compounds examined give a reddish-brown ppt. of $Fe(OH)_3$ in <0.5 min. when a 10-mg. sample is mixed with 7 c.c. of a solution of 25 g. of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in 500 c.c. of $H_2O + 2$ c.c. of conc. H_2SO_4 , followed by the addition of 5 c.c. of 15% $EtOH-KOH$ after removal of air by a stream of inert gas. 75 compounds not containing NO_2 gave negative results; exceptions are NO -compounds, aliphatic nitrates and nitrites, quinones, and NH_2OH . F. N. W.

Simultaneous determination of methoxyl and ethoxyl in organic substances. M. PHILLIPS and M. J. GOSS (J. Assoc. Off. Agric. Chem., 1937, 20, 292—297).— MeI and EtI produced as in Zeisel's method are converted with NMe_4I and NMe_3EtI , which are separated by the Willstätter-Uttinger method (cf. A., 1911, i, 659). E. C. S.

Relative reactivities of organo-metallic compounds. XVI. Detection of the SH group. H. GILMAN and J. F. NELSON (J. Amer. Chem. Soc., 1937, 59, 935—937; cf. this vol., 221).— $BiEt_3$ and $PbEt_4$ are diagnostic of SH, since they react, though not quantitatively, therewith, but not appreciably with OH, NH, $C\equiv CH$, $CH_2Ac \cdot COMe$, Ph_2N_2 , $PhNO_2$, $C_6H_4(NO_2)_2$, $C_6H_3(NO_2)_3$, or Et_2S_2 . Acids also react (with $BiEt_3$ < with $PbEt_4$), the amount of reaction with strong acids, e.g., $CCl_3 \cdot CO_2H$, approaching that with SH. Both reagents indicate SH in $MeCS \cdot OH$ and 1-thiolbenzthiazole; the thiazole, however, does not react with $BiPr^a_3$. Some SH is indicated in $CS(NHPh)_2$, but not in $CS(NH_2)_2$. $BiEt_3$ reacts with traces of O_2 and may be a reagent for O_2 . R. S. C.

Manometric micro-titration with ferricyanide. E. HAAS (Biochem. Z., 1937, 291, 79—80).—When H in an org. compound (e.g., glutathione, dihydropyridine nucleotide) in neutral solution containing HCO_3^- is oxidised by $K_3Fe(CN)_6$, 1 mol. of CO_2 is produced for each H atom oxidised. Hence such compounds are determined in the Warburg apparatus in an atm. of CO_2 (10 vols.) and A (90 vols.) with accuracy > that of other methods. W. McC.

Determination of alcohol by Widmark's method. E. FLOTOW (Pharm. Zentr., 1937, 78, 389; cf. A., 1936, 1359).—Improvements in the acid-dichromate method are described. E. H. S.

Micro-determination of tert.-butyl alcohol. A. LINDENBERG (Compt. rend. Soc. Biol., 1937, 125, 135—138).—The complex obtained by heating in a sealed tube with Deniges' reagent is decomposed with HCl and excess titrated. H. G. R.

Azides. VIII. β -Naphthazide as a reagent for identification of primary and secondary amines. P. P. T. SAH (J. Chinese Chem. Soc., 1937, 5, 100—106).— β -Naphthazide, prepared by condensing Et β -naphthoate with N_2H_4 hydrate and diazotising in AcOH, readily reacts in hot C_6H_6 with alcohols, phenols, amines, amides, and aldoximes. The following derivatives β - $C_{10}H_7$ ·NH·CO·NHR were prepared, with the m.p. (corr.) given: from NH_2 ·R: phenyl-, 236—238°, o-tolyl-, 232—233°, m-tolyl-, 222—223°, p-tolyl-, 266—267°, p-xylyl-, 245—247°, p-diphenyl-, 259—260°, α -naphthyl-, 249—250°, β -naphthyl-, 310—312°, o-nitrophenyl-, 203—205°, m-nitrophenyl-, 222—223°, p-nitrophenyl-, 275—276°, p-bromophenyl-, 286—288°, p-chlorophenyl-, 280—281°, m-bromo-p-tolyl-, 230—232°, m-nitro-p-tolyl-, 220—221°, o-nitro-p-tolyl-, 217—218°, o-hydroxyphenyl-, 191—193°, p-hydroxyphenyl-, 255—256°, o-carboxyphenyl-, 213—214°, m-carboxyphenyl-, 277—278°, p-carboxyphenyl-, 291—292°, benzoyl-, 223—224°, acetyl-, 305—306°, p-aminophenyl- (>320°), p-amino-p-diphenyl- (>320°), n-octyl-, 98—99°, and o-carbethoxyphenyl-, 165—167°; from $NHRR'$: diphenyl-, 157—158°, acetylphenyl-, 311—312°, and phenylmethyl-, 153—155°. A. LI.

Identification of the amino-acids: p-toluene-sulphonyl chloride as a reagent. E. W. McCHESNEY and W. K. SWANN, jun. (J. Amer. Chem. Soc., 1937, 59, 1116—1118).—p- C_6H_4 Me·SO₂ derivatives of the following are described: dl-, m.p. 138—139°, and d-alanine, m.p. 132—133°, l-cystine (disubstituted), m.p. 201—203° (decomp.), glycine, m.p. 147°, l-histidine, m.p. 202—204°, l-hydroxyproline, m.p. 153°, dl-, m.p. 139—140°, and d-isoleucine, m.p. 130—132°, l-leucine, m.p. 121—122°, dl-methionine, m.p. 104—105°, dl-norleucine, m.p. 124°, dl-, m.p. 134—135°, and l-phenylalanine, m.p. 161°, dl-serine, m.p. 212—213° (decomp.), l-tyrosine (disubstituted), m.p. 113—114°, and d-valine, m.p. 147°. The l-aspartic and d-glutamic acid derivatives are oils, but give Bu₂ esters, m.p. 61—62° and 64—65°, respectively. The dl-lysine and l-proline derivatives are oils, but give Bu esters, m.p. 111—113° and 53—55°, respectively. The oily derivative of d-arginine gives an oily Bu ester. R. S. C.

Physical aspects of colorimetric determination [of cholesterol] by the Liebermann-Burchard reaction. R. LATARJET and A. HUSSON (Compt. rend. Soc. Biol., 1937, 125, 683—686).—Spectrophotometric observations indicate the correct proportion of reagents and that the colour is stable for 30—45 min. H. G. R.

Identification of allylbarbiturates. M. PESEZ (J. Pharm. Chim., 1937, 59, 508—514).—20—30 mg. of diallylbarbituric acid are shaken with 2 c.c. of conc. H_2SO_4 , treated with 2 drops of a solution of KBr (2 g.) and $KBrO_3$ (0.5 g.) in H_2O (20 c.c.), warmed for 5 min. at 100°, and cooled. Addition of 2 drops of a solution of o-OH- C_6H_4 ·CO₂Me, cresopyrin, or guaiacol gives a reddish-violet (becoming intense rose in a few sec. at 100° and then reddish-brown), rose, or deep violet (becoming wine-red) colour, respectively. iso-Propyl- and -butyl-allylbarbituric acid give with

these phenols violet, sky-blue (becoming dark blue when heated), and pale blue colours, respectively, and with thymol a red, with codeine a violet-blue, with β - $C_{10}H_7$ ·OH an emerald-green, and with resorcinol a blood-red (green fluorescence) colour. 0.1 mg. gives the test. Substances normally present in drugs and extracted by Et_2O , including other barbiturates, do not interfere. The reaction depends on the changes: CH_2 :CH·CH₂· \rightarrow CH_2 Br·CHBr·CH₂· \rightarrow OH·CH₂·CH(OH)·CH₂· \rightarrow CHO·CO·CH₂·, and condensation of the glyoxal with the phenol. R. S. C.

Colorimetric determination of uric acid. A. KERN and E. STRANSKY (Biochem. Z., 1937, 290, 419—427).—Various methods for colorimetric determination of uric acid (I) are critically investigated. The uranyl acetate method is preferred for deproteinisation, and isolation of (I) is found to be unnecessary with serum. Glucose in amounts >6 mg. per c.c. interferes with the determinations but glutathione up to 1 mg. per c.c. has no effect. By use of a new reagent consisting of a 10% solution of Na_2SiO_3 + glycerol, the colour max. can be maintained for 1 hr. without turbidity appearing. P. W. C.

Colour reaction of morphine and alkaloidal derivatives [thereof]. M. PESEZ (J. Pharm. Chem., 1937, [viii], 25, 504—508).—When 0.1 c.c. of 10% aq. KBr is added to 10—20 mg. of morphine (I) in 2 c.c. of conc. H_2SO_4 and the solution is warmed at 100° for 3 min., a yellowish-brown to -green colour develops; the solution is cooled and 20 c.c. of distilled H_2O are cautiously added, giving a pale to emerald-green colour. The reaction is positive with a few tenths of a mg. of (I). Large amounts give an amorphous green ppt., sol. to green or blue solutions in MeOH, EtOH, $COMe_2$, and $CHCl_3$, sparingly sol. in Et_2O , C_6H_6 , and EtOAc; the colour is removed from the aq. solution by these solvents. Saturated Br- H_2O , but not KCl, KI, KIO_3 , or $KOCl$, may be used. Codeine, dionin, heroin, and peronin give the same colour; thebaine gives a green with a bluer shade; narcotine, narceine, apomorphine, papaverine, colchicine, hydrastine, and other alkaloids and glucosides give no or different colours. Sugars interfere, but are removed by treating the mixture with NH_3 and extracting the (I) with $CHCl_3$. R. S. C.

Mannich's method for determination of morphine. J. R. NICHOLLS (Analyst, 1937, 62, 440—443; cf. A., 1935, 507).—30% aq. EtOH is substituted for aq. MeOH, and aq. NH_3 is substituted for NaOH in the original method. The method, in either form, does not give accurate results with opium since other phenolic alkaloids interfere. E. C. S.

Principal chemical tests for morphine. C. C. FULTON (Amer. J. Pharm., 1937, 109, 219—240).—A review. J. D. R.

Quantitative, spectrographic determination of quinine and cinchonine in mixtures of the two. L. FUCHS and A. KAMPITSCH (Sci. pharmaceutica, 1935, 6, 125—132; Chem. Zentr., 1936, i, 3365).—Solutions in 0.1N- H_2SO_4 obey the Lambert-Beer law and absorption spectra may be used for this determination. Curves, diagrams, and tables are given. H. N. R.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1937.



Changes of configuration during reactions at singly and doubly bound carbon atoms. E. BERGMANN [with Y. SPRINZAK] (Helv. Chim. Acta, 1937, 20, 590—621).—If a polar mol. C-X reacts with a negatively-charged ion Y the latter approaches the dipole C-X at the positive side and reacts with expulsion of X as negative ion: $Y' + CRR'R''X \rightarrow Y-CRR'R'' + X'$. Spatially therefore Y occupies a position of the tetrahedron diametrically opposite to that of the substituent X; a Walden transformation occurs. Conversely a positive ion approaches the polar linking from the negative side, giving a neutral mol. and a positive carbonium radical which becomes stabilised with maintenance of configuration if the stability of the configuration within it is great and with partial or complete racemisation if the stability is small; a Walden inversion never occurs. From this viewpoint the following instances of racemisation have been investigated: CHMeBuBr by LiBr in abs. EtOH; $CO_2Me \cdot CHCl \cdot CH_2 \cdot CO_2Me$ by LiCl in abs. CO_2Me ; $CO_2Me \cdot CHBr \cdot CH_2 \cdot CO_2Me$ by LiBr in CO_2Me ; CHMeBuI by NaI in CO_2Me and binary solvents containing CO_2Me . The conception of racemisation as a substitution process is strengthened by the similarity of the change with other bimol. reactions of the type $C-X + Y' \rightarrow CY + X'$, by analogy in the behaviour of I' towards C-I and towards C-F, C-Cl, and C-Br, by the identity in the rate of substitution in the systems, org. iodide + radioactive I' and optically active org. iodide + I', and by the influence of the medium on the reaction. It follows, therefore, that the reaction between an optically active halide and the salt of an org. acid must be accompanied by a Walden inversion whereas the esterification of an optically active alcohol occurs without configurational change. Inversion also accompanies the reaction between optically active halide and sodiomalonic esters or metal alkyls. Instances of positive mechanism are discussed. The addition of halogen to the ethylenic linking is represented: $Br' + C:C \rightarrow Br-C-C-$ and $Br-C-C + Br \rightarrow Br-C-CBr + Br'$ or $Br + C:C \rightarrow Br-C-C^+$ and $Br-C-C^+ + Br_2 \rightarrow Br-C-CBr + Br'$. Reactions appear to occur according to both schemes; the negative mechanism converts *cis-trans* isomeric ethylenes into epimeric halides whereas positive mechanism leads either to one form of the additive product or to a mixture of both. Both mechanisms explain diene addition: $Br^- + C:C:C:C \rightarrow Br-C-C-C:C$ (I); (I) + $Br_2 \rightarrow CBr-CBr-C:C + Br^-$ and $Br^- + C:C:C:C \rightarrow Br-C-C-C-C-$ (II), (II) + $Br_2 \rightarrow Br-C-C-C-CBr + Br^-$. A third mechanism, $Br + C:C \rightarrow Br-C-C^{\bullet}$ (III); (III) + $Br_2 \rightarrow CBr-CBr + Br$, involves uncharged radicals

and is applicable to the halogenation of gaseous ethylenes in light. All methods differ in the mechanism from catalytic hydrogenation, which is due to mol. H_2 and is characterised by *cis*-addition and 1:2 not 1:4 reaction in the case of dienes. Addition of halogen is never a mol. reaction; it does not take place by simple opening of a linking and addition at the liberated valency (*cis*-reaction) but is accompanied by isomerisation (*trans*-addition). Reduction of an ethylene with nascent H has the same characteristics as bromination with Br atoms; the intermediate product can be the carrier of a *cis-trans* isomerisation. The following compounds appear new: α -methylamyl bromide, b.p. 143—144°, and its optically active isomeride, $[\alpha]_D +20.1^\circ$ in CO_2Me ; $Me_2(-)$ -bromo-succinate, b.p. 87°/2.5 mm., $[\alpha]_D -58.5^\circ$ in CO_2Me ; $Et_2 \alpha$ -phenylethylmalonate, b.p. 138°/1.5 mm., $[\alpha]_D -6.55^\circ$; α -phenylethylmalonic acid, m.p. 142—143°; β -phenylbutyric acid, b.p. 140—141°/2 mm.; (+)-phenylmethylcarbinyl acetate, b.p. 104—105°/23 mm., $[\alpha]_D +6.44^\circ$, from (—)-CHPhMeCl and AgOAc or NaOAc; phenylmethylcarbinyl Et ether, b.p. 74—76°/23 mm., $[\alpha]_D -25.2^\circ$ in CO_2Me ; (+)- β -chloro- Δ^2 -pentene, $[\alpha]_D +3.0^\circ$ in Et_2O ; (—)- Δ^2 -penten- β -ol, $[\alpha]_D -3.1^\circ$; (—)- β -chloro- Δ^2 -pentene (IV), $[\alpha]_D -5.4^\circ$ in Et_2O ; $\alpha\alpha$ -diphenyl- β -methyl- Δ^2 -pentene, b.p. 174°/20 mm., $[\alpha]_D \pm 0^\circ$ in Et_2O or EtOH [from (IV) and $CHPh_2Na$]; β -benzhydrylpentane, b.p. 160—162°/14 mm.; $Et_2 \beta$ - Δ^2 -pentenylmalonate, b.p. 130°/20 mm., $[\alpha]_D \pm 0^\circ$; β -methyl- Δ^2 -hexenoic acid, b.p. 109—110°/15 mm.; β -methylhexoic acid, b.p. 116°/15 mm.

H. W.

Selectivity of iodic acid in the oxidation of organic compounds. R. J. WILLIAMS and M. A. WOODS (J. Amer. Chem. Soc., 1937, 59, 1408—1409).—With KIO_3 in 40% H_2SO_4 (the liberated I being removed by steam and the remaining KIO_3 titrated), the following are oxidised (using ≤ 4 equivs. of KIO_3 per mol.): aliphatic alcohols (up to C_8) except MeOH, polyhydric alcohols with non-adjacent hydroxyls, aliphatic and aromatic aldehydes, CO_2Me , CO_2MeEt , and CPhMe, fructose, sorbose, sucrose, *d*-arabinose, *l*-xylose, and rhamnose, phenols and their ethers, and NH_2Ph derivatives. The following are unaffected: polyhydric alcohols with adjacent hydroxyls, CPh $_2$, benzil and benzoin, aliphatic and aromatic acids, unsaturated and α -OH-acids, protein NH_2 -acids except cystine, tyrosine, and tryptophan, and aldohexoses.

A. LI.

Kinetics and mechanism of decomposition of hydrocarbons. IV. Influence of pressure on the velocity and direction of decomposition of

ethane. A. I. DINTZES, V. R. SHARKOVA, A. V. SHERKO, and A. V. FROST (J. Gen. Chem. Russ., 1937, 7, 1063—1070).— C_2H_6 decomposes at 635° as follows: $2H + 2C_2H_4 \leftarrow 2C_2H_6 \rightarrow 2CH_4 + C_2H_4$; the latter reaction is favoured by increasing pressure from 1 to 26 atm.

R. T.

Pyrolysis of ethane.—See A., I, 466.

Unimolecular olefine formation from alkyl halides.—See A., I, 467.

Mechanism of substitution at a saturated carbon atom. VII—X.—See A., I, 467.

Dielectric constant and molecular size of duprene and rubber hydrochloride.—See A., I, 397.

Alkyl acetylenes and their addition compounds. XIX. Preparation and alkylation of metal acetylides in liquid ammonia. T. H. VAUGHN, G. F. HENNION, R. R. VOGT, and J. A. NIEUWLAND (J. Org. Chem., 1937, 2, 1—22).—Prep. of metal acetylides by passing C_2H_2 into a solution of the metal in liquid NH_3 is very slow. It is difficult to determine the end-point if the metal amide is used. C_2H_2 at 100—250 lb. per sq. in. acts rapidly but dangerously. The best method of prep. is to pre-cool the NH_3 by evaporation by a rapid stream of C_2H_2 , thus obtaining a cold conc. solution, and to add thereto the metal in liquid NH_3 with stirring without allowing the bulk of the solution to become blue. 5 mols. of Na are thus converted into $NaHC_2$ in 40 min. KHC_2 , CaH_2C_4 , and BaH_2C_4 are similarly prepared. The Ca and, more so, Ba salts are unstable, the latter not being obtained pure. Thus prepared, the salts contain a little oxide and hydroxide and (?) traces of amide. The interaction of these salts with alkyl halides and sulphates at room temp./100—250 lb. per sq. in., about $-34^\circ/1$ atm., and about $-34^\circ/25$ lb. per sq. in., in 2, 12, and 30 g.-mol. batches is described and modifications of the methods are discussed. Yields varied from 0 to 100%, but were usually \ll theoretical. Much of the loss is proved to be due to entrainment during removal of the solvent NH_3 and is avoidable by a modified procedure. For Me and Et, sulphates give the best crude yields of Δ^a -alkinenes, but bromides are generally preferable as they react more rapidly than chlorides and give smaller amounts of amines than do iodides or sulphates. The nature of the metal is relatively unimportant, but for the prep. of $C_5H_{11} \cdot C \equiv CH$ under comparable conditions yields are K 54, Na 50, Ba 41, and Ca 31. The alkinene obtained is difficult to free from small amounts of halide, particularly the bromide. Other products formed and more easily removed are olefines (traces only of C_2H_4 , 8—20% of Δ^a -pentene; cyclohexyl bromide gives moderate yields of cyclohexene and no $C_6H_{11} \cdot C \equiv CH$), amines (formed particularly from the chlorides and at room temp.; removed by washing first with dil. HCl and then with H_2O), C_2H_2 (2—17%), alcohols (1—10%) and ethers (1—5%) (formed by traces of NaOH thus: $NaOH + RX \rightarrow ROH$; $ROH + NaHC_2 \rightarrow C_2H_2 + RONa$; $RONa + RX \rightarrow R_2O + NaX$), dialkylacetylenes R_2C_2 , and probably $CH \equiv C \cdot CMe_2 \cdot OH$ (derived from $COMe_2$ in the C_2H_2). R_2C_2 are formed by way of

$CR \equiv CNa$, and not Na_2C_2 ; the isolation of $CR \equiv CNa$ and its reaction with alkyl halides and sulphates to give $CR \equiv CR'$ in fair yields are described. Δ^a -Decinene, b.p. 105.2 — $105.8^\circ/79$ mm., $172^\circ/745$ mm., Δ^b -dodecinene, b.p. 97 — $98^\circ/16$ mm., $209^\circ/745$ mm., Δ^b -heptinene, b.p. 107 — $111^\circ/750$ mm., Δ^b , b.p. 130.4 — $130.6^\circ/745$ mm., Δ^c , b.p. 127 — $130^\circ/750$ mm., and Δ^b -octinene, b.p. 131 — $135^\circ/750$ mm., Δ^b , b.p. 150 — $154^\circ/750$ mm., and Δ^c -noninene, b.p. 150 — $154^\circ/750$ mm., are described (n and d given). The possibility of wandering of the acetylenic linking, particularly at the higher temp., is discussed.

R. S. C.

Dialkylacetylenes. E. A. BRIED and G. F. HENNION (J. Amer. Chem. Soc., 1937, 59, 1310—1311).—The following dialkylacetylenes were prepared by slowly adding the alkyl bromide to a well-stirred mixture of C_2Na_2 , NH_2Na , and liquid NH_3 : Et_2 , b.p. $81.5^\circ/744$ mm., Pr_2 , b.p. $130^\circ/744$ mm., Bu_2 , b.p. $115.9^\circ/115$ mm., $diamyl$, b.p. $115^\circ/30$ mm.; and $ethylbutyl$, b.p. $131.8^\circ/737$ mm., by successively adding $BuBr$, NH_2Na in liquid NH_3 (after 3 hr.), and $EtBr$ (after $\frac{1}{2}$ hr.) to a solution of C_2Na_2 in liquid NH_3 .

A. LI.

Rearrangements of polyacetylenes. X. Rearrangement product of hexatert.-butylacetylenylethane. W. J. SPARKS, W. J. PEPPEL, and C. S. MARVEL (J. Amer. Chem. Soc., 1937, 59, 1351—1352).—Hexatert.-butylacetylenylethane, when heated in $EtOH$, isomerises to a compound (I) {dibromide, m.p. 169 — 170° [reconverted by KOH into (I)], dichloride, m.p. 161° }, rapidly reduced (PtO_2 — Pt -black) to a viscous hydrocarbon, $C_{38}H_{70}$ (corresponding with a reduction of 4 triple linkings), which can absorb 8 Br per mol.; similar reduction of $(C_4Bu \equiv C)_3C \cdot OH$ yields tri-($\gamma\gamma\gamma$ -trimethyl- n -propyl)-carbinol, m.p. 44 — 45° . Oxidation of (I) with O_3 followed by H_2O_2 affords Bu^*CO_2H , whilst CrO_3 gives an oxidation product apparently identical with that of the dimeride of $(C_4Bu \equiv C)_3CCl$. These facts suggest that (I) is the diallene $[(C_4Bu \equiv C)_2C \equiv C \cdot C_4Bu^*]_2$.

A. LI.

Hydrolysis and alcoholysis of alkyl halides.—See A., I, 417.

Fluorinated derivatives of methane. A. L. HENNE (J. Amer. Chem. Soc., 1937, 59, 1400).—The b.p. of the following have been accurately determined: $CHCl_2F$, 8.9 — 9.0° , $CHClF_2$, -40.8° to -40.6° , CH_2ClF , -9.0° to -9.1° , CH_2F_2 , -51.6° . The difluorides are chemically and physiologically inert, but the monofluorides give the usual halide reactions (with difficulty) and are weak anaesthetics.

A. LI.

Fluoroform. A. L. HENNE (J. Amer. Chem. Soc., 1937, 59, 1200—1202).— CHF_3 , prepared by warming $CHBr_3$ with Br and excess of SbF_3 at 4 atm., and treating the resulting $CHBrF_2$, after purification, with HgF_2 (at 12 atm., cooled in solid CO_2), is chemically and physiologically inert, but reacts with F_2 at room temp., Cl_2 in bright sunlight, or CaO at red heat.

A. LI.

Fluorocarbons. J. H. SIMONS and L. P. BLOCK (J. Amer. Chem. Soc., 1937, 59, 1407).—Fractionation of the reaction mixture of C and F_2 yields CF_4 , C_2F_6 , C_3F_8 , f.p. -183° , b.p. -36° , C_4F_{10} , f.p. -84.5° , b.p.

4° , C_6F_{12} , f.p. -10° , b.p. 30° , and C_6F_{14} , f.p. -4° , b.p. 60° , identified by their mol. wts. A. LI.

Reaction kinetics and Walden inversion. I. Homogeneous hydrolysis and alcoholysis of β -*n*-octyl halides. E. D. HUGHES, C. K. INGOLD, and S. MASTERMAN. II. Homogeneous hydrolysis, alcoholysis, and ammonolysis of α -phenylethyl halides. E. D. HUGHES, C. K. INGOLD, and A. D. SCOTT. III. Homogeneous hydrolysis and alcoholysis of α -bromopropionic acid, its ester and anion. W. A. COWDREY, E. D. HUGHES, and C. K. INGOLD. IV. Action of silver salts in hydroxylic solvents on β -*n*-octyl bromide and α -phenylethyl chloride. E. D. HUGHES, C. K. INGOLD, and S. MASTERMAN. V. Action of silver salts in hydroxylic solvents on α -bromopropionic acid, its methyl ester, and sodium salt. W. A. COWDREY, E. D. HUGHES, and C. K. INGOLD. VI. Relation of steric orientation to mechanism in substitutions involving halogen atoms and simple or substituted hydroxyl groups. W. A. COWDREY, E. D. HUGHES, C. K. INGOLD, S. MASTERMAN, and A. D. SCOTT (J.C.S., 1937, 1196—1201, 1201—1208, 1208—1236, 1236—1243, 1243—1252, 1252—1271).—I. Evidence showing that β -*n*-octyl alcohol, chloride, bromide, and iodide with the like sign of rotation have corresponding configurations is summarised. Hydrolysis of the bromide by *N*-KOH in 60 vol.-% aq. EtOH at the b.p. yields inverted alcohol of high optical purity, mainly by a bimol. reaction. In absence of KOH (0—0.3*N*-HBr) hydrolysis takes place exclusively by a unimol. mechanism ($RBr \rightarrow R' + Br^-$), yielding an inverted product of lower optical purity. Inversion also occurs in the alcoholysis (with NaOEt) of both the bromide and chloride. The unimol. mechanism involves much more racemisation than does the bimol. Optically pure β -*n*-octyl bromide is calc. to have $[\alpha]_D^{25}$ 33.8°.

II. Hydrolysis of CHPhMeCl in H_2O or aq. COMe₂, whether in presence of KOH or of HCl, is exclusively unimol., and yields an inverted product of low optical purity. Alcoholysis by MeOH or EtOH gives a similar result, whereas if brought about by Na alkoxides the reaction is chiefly bimol. and gives an ether with inverted configuration and high optical purity. Inversion also occurs in ammonolysis. In the unimol. hydrolysis racemisation increases as the H_2O is diluted with inert COMe₂.

III. Hydrolysis of CHMeBr·CO₂H in dil. aq. H₂SO₄ is bimol. (though experimentally of first order) and yields an inverted product of high optical purity. A similar result is obtained in the methoxylation of the Me ester. Substitution of OH or OMe in the anion is bimol. when effected by OH' or OMe', but unimol. when effected by H_2O or MeOH. In the former case there is approx. complete inversion, whilst in the latter the original configuration is retained.

IV. Substitution of OH and OEt in C₈H₁₇Br in aq. EtOH by means of Ag₂O, AgNO₃, or AgOAc, and of OH in CHPhMeCl by Ag₂O leads in every case to products with inverted configuration. The main difference is that in the heterogeneous reactions the retention of optical purity is > that in the homogeneous unimol. reactions. In hydrolysis of

CHPhMeCl racemisation increases markedly on diluting the H_2O with COMe₂.

V. Experiments similar to those described in (III), but using Ag₂O, AgNO₃, and Ag₂CO₃, show inversion to be the predominant effect with the Me ester and a substituted amide of CHMeBr·CO₂H, and retention of the original configuration with the anion. Racemisation occurs in all cases. In all these reactions, including those of (IV), the reagent is Ag⁺ adsorbed on AgBr, Ag₂O, or both.

VI. General principles relating to the orientation of substitution, in the case of reciprocal replacements of halogen and OR, are advanced. F. L. U.

Dehalogenation of organic iodo-compounds by hydrogenation in alkaline medium; simple determination of small quantities of organic iodine. J. A. GAUTIER (Bull. Soc. chim., 1937, [v], 4, 219—225).—Many org. I-compounds are readily and completely dehalogenated by boiling with Zn and about *N*-NaOH, or Zn and *N*-KOH-EtOH if insol. in aq. NaOH. On neutralisation the excess of Zn is pptd. as hydroxide which carries with it some of the decomp. products. The I (as ZnI₂) is best determined by the method of Bernier *et al.* (A., 1911, ii, 435). Good results are obtained with aliphatic and aromatic compounds, except with certain iodinated oils the hydrogenation products of which are difficult to filter, but heterocyclic I-compounds are not completely dehalogenated by this method. H. G. M.

Hydrolysis of carbon tetraiodide. M. S. KHARASCH, W. G. ALSOP, and F. R. MAYO (J. Org. Chem., 1937, 2, 76—83).—Cl₄ is stable in EtOH, MeOH, Bu'OH, C₆H₆, CHCl₃, etc. in absence of O₂. In presence of O₂, it decomposes at various rates in these solvents, but, presumably because of its insolubility, not in H_2O or aq. KOH. KOH-MeOH decomposes both Cl₄ and CHI₃. CaO- and NaOPh-MeOH decompose Cl₄, but not CHI₃; with these reagents Cl₄ gives I', but no CHI₃, which is thus not a decomp. product of Cl₄. Cl₄ is destroyed by KOH-aq. MeOH-O₂; the amount of I formed depends on the amount of KOH, with 6 mols. of KOH no I, but much I', and with 1 mol. much I and little I', being obtained. There is thus no evidence for the existence of "positive I" in Cl₄ or other iodomethanes; reports to the contrary are due either to the physical resemblance of CHI₃ and recovered Cl₄ or to the fact, established by a series of experiments, that the presence of traces of CH₂O or MeCHO in aq. EtOH-KOH may lead to formation of large amounts of CHI₃. Exact duplication of results is not anticipated, as the rates of decomp. are probably affected also by the age and purity of the Cl₄, peroxide content of the solvent and aldehyde, temp., illumination, and agitation. R. S. C.

Thermal decomposition of ethylene dibromide.—See A., I, 466.

Determination of unsaturation of chloroprene polymerides. II. A. L. KLEBANSKI and M. RACH-LINA (J. Gen. Chem. Russ., 1937, 7, 1299—1305).—Theoretical vals. are obtained for the I vals. of chloroprene rubber in CCl₄, using a 140% excess of ClI, also in CCl₄. The I vals. fall with increasing complexity

of the polymerides (from α - to μ -). The chloriodides do not undergo hydrolysis under the conditions of the determination, so that the acidity developed is ascribable to substitution. (Cf. A., 1936, 962.) R. T.

Hydrolysis of dichlorobutanes in presence of sodium carbonate and hydrogen carbonate, under pressure. A. F. DOBRIANSKI, R. GUTNER, and M. SČTŠCHIGELSKAJA (J. Gen. Chem. Russ., 1937, 7, 1315—1320).—(CHMeCl)₂ and 6—12% NaHCO₃ or 8% Na₂CO₃ at 135—195° yield CHMe:CMcCl (I), (CHMe·OH)₂, COMeEt, CH₂:CH·CHMe·OH, and CHMe:CH·CH₂·OH. The products obtained analogously from CH₂Cl·CH₂Cl are as above, except that the glycol is OH·CH₂·CH₂·OH. CH₂Cl·CMcCl yields OH·CH₂·CMc·OH, CHCl:CMc₂ (II), and Pr³CHO. The yield of glycol is inversely, and of (I) or (II) directly, \propto [NaHCO₃]. R. T.

Aliphatic chloro-derivatives. X. Action of chlorine on Δ^a - and Δ^b -pentenes. D. TISCHTSCHENKO and M. SČTŠCHIGELSKAJA (J. Gen. Chem. Russ., 1937, 7, 1246—1248).— Δ^b -Pentene and Cl₂ yield a mixture of diastereoisomeric $\beta\gamma$ -dichloropentanes, b.p. 140—141° and 143—144°; Δ^a -pentene similarly gives $\alpha\beta$ -dichloropentane, b.p. 148.4—148.8°, with about 1% of a monochloropentene in both cases. The presence of substances binding HCl (CaCO₃, CaO, KOH) does not affect the result. R. T.

Higher $\omega\omega'$ -dihalogeno-compounds. II. $\alpha\mu$ -Dibromododecane from adipic acid. J. VON BRAUN and A. VON FRIEDRICH-LIEBENBERG (Ber., 1937, 70, [B], 1598—1602; cf. this vol., 270).—The optimal conditions have been worked out for the scheme: Br·[CH₂]₆·Br \rightarrow OPh·[CH₂]₆·Br \rightarrow OPh·[CH₂]₁₂·OPh \rightarrow C₆H₁₁·O·[CH₂]₁₂·O·C₆H₁₁ \rightarrow Br·[CH₂]₁₂·Br. In the first stage Br·[CH₂]₆·Br and NaOPh (1.5 : 1) are allowed to interact in EtOH and the mixture of OPh·[CH₂]₆·OPh and NaBr is filtered. The filtrate is distilled and the mixture of Br·[CH₂]₆·Br and Br·[CH₂]₆·OPh separated by a single fractionation. Fourfold treatment of the bromide rapidly gives an approx. 85% yield of the Br-ether. OPh·[CH₂]₁₂·OPh containing OPh·[CH₂]₆·OPh is not isolated by distillation but merely washed with EtOH, whereby OPh·[CH₂]₆·OPh is not removed; this is best effected after hydrogenation, when a single distillation suffices. C₆H₁₁·O·[CH₂]₁₂·O·C₆H₁₁ is more conveniently converted into Br·[CH₂]₁₂·Br by repeated treatment with boiling 48% HBr in open vessels than by use of fuming HBr under pressure. $\alpha\zeta$ -Dicyclohexyloxyhexane, b.p. 194°/13 mm., ζ -phenoxyhexyl bromide, b.p. 172—174°/13 mm., and $\alpha\mu$ -dicyclohexyloxydodecane, b.p. about 260°/13 mm., appear new. H. W.

Preparation and reactions of α -halogenoalkenes. P. A. MCCUSKER and R. R. VOGT (J. Amer. Chem. Soc., 1937, 59, 1307—1310).— α -Bromo- Δ^a -heptinene is prepared by refluxing MgEtBr with heptinene in Et₂O, adding Br at -32°, and hydrolysing with dil. HCl. α -Chloro- Δ^a -heptinene [prepared by adding heptinene to KNH₂ in liquid NH₃, replacing the NH₃ by Et₂O, passing in Cl₂ at -70°, and hydrolysing with H₂O] with KCN in aq. MeOH gives C₆H₁₁·C(OMe):CH·CN. Chloro- and bromo-heptinene add MeOH in presence of BF₃, giving α -chloro-, b.p.

80—82°/8 mm., and α -bromo-, b.p. 88°/5 mm., $\beta\beta$ -dimethoxyheptane. A. LI.

Determination of ethyl alcohol in presence of acetone. C. R. HOSKINS (Analyst, 1937, 62, 530—533).—COMe₂ is removed by pptn. with excess of acid HgSO₄ in presence of HCO₂Na at 80°, excess of Hg pptd. by K₂C₂O₄, and the EtOH distilled. The loss of EtOH varies from 0.4 to 1.3%. E. C. S.

Diamagnetism of iodine solutions and the purity of alcohol.—See A., I, 459.

Exchange reactions in deuterioalcohol. M. S. KHARASCH, W. A. BROWN, and J. McNAB (J. Org. Chem., 1937, 2, 36—48).—EtOH, containing 9.1 mol.-% of EtOD, is obtained by treating abs. EtOH with D₂O and later heating with CaO and distilling. Exchange of H for D by various substances in this solvent under various conditions is investigated by burning 1 g. of the residual EtOH-EtOD and determining by flotation the d of the H₂O formed. No exchange takes place with acenaphthene, CH₂Ph₂, CHPh₃, or β -C₁₀H₇·OMe. No exchange occurs with fluorene, CHPh(C₆H₄·OMe)₂, p -C₆H₄Me·NO₂, or 1 : 3 : 5-C₆H₃(NO₂)₃ unless 0.02M-NaOH is present. Exchange occurs with o -C₆H₄Me·NO₂ and 7 : 8-benzoquinoline, but more so in the presence of 0.02M-NaOH. Some exchange occurs with m -C₆H₄Me·NO₂, but this is unaffected by NaOH and may be due to an impurity. Exchange occurs with CH₂Ac·CO₂Et (slightly >1H), succinimide (1H), and quinoline (2H). Exchange occurs with NPhMe₂, unaffected by 0.02M-NaOH, but much increased by 0.01M-H₂SO₄. The results do not represent equilibrium vals.; they are discussed with particular reference to NPhMe₂, the result with which is held to be due to the high electro-negativity of o - and p -C₆H₄·NMe₂. Possible mechanisms of the exchange are discussed. R. S. C.

Aluminium isopropoxide as reducing agent. General method for reduction of carbonyl. H. LUND (Ber., 1937, 70, [B], 1520—1525).—Reduction of :CO to :C·OH is effected by Al(OPr³)₃ in boiling Pr³OH or C₆H₆ in an apparatus arranged so that the COMe₂ formed is volatilised without too great distillation of Pr³OH; the end is reached when the distillate does not give a ppt. with 2 : 4'-(NO₂)₂C₆H₃·NH·NH₂ in HCl. The method is widely adapted to the reduction of aldehydes and ketones to the corresponding alcohols, side reactions being seldom observed. It cannot be extended to ketones which readily become enolised (CH₂Bz₂, CH₂Ac·CO₂Et, etc.) or to phenolic ketones or CO-acids which give Al salts insol. in Al(OPr³)₃. Examples are cited of the reduction of NO₂-ketones and -aldehydes to the corresponding NO₂-alcohols but the invariable non-reducibility of ·NO₂ is not established. Simply and multiply unsaturated ketones are normally reduced to the corresponding carbinols but their isolation is hampered by the facility with which they afford Pr³ ethers. CPh·CH₂Br is smoothly reduced to phenylbromomethylcarbinol, b.p. 133—134°/12 mm., and CBr₃·CHO to CBr₃·CH₂·OH (yield 77%). 2-Naphthylmethylcarbinol, m.p. 72°, m -nitrophenylmethylcarbinol, m.p. 62.5°, and p -nitrobenzhydrol, m.p. 74°, appear new. H. W.

Racemisation experiments with vapours of substances difficult to racemise. U. VON WEBER (Z. physikal. Chem., 1937, 179, 295—306).—There is no racemisation when the vapour of *d*-amyl alcohol or *d*-CHMeEtPr under 0.5 atm. is heated even at temp. at which decomp. begins to be appreciable. The absence of reaction is probably due to the const. of action being very low. R. C.

Determination of sorbitol. J. JEANPRÉTRE (Mitt. Lebensm. Hyg., 1937, 28, 87—91).—Litterscheid's method for the detection of sorbitol (B., 1932, 281) can be made approx. quant. in absence of excess of mannitol (I). (I) is largely removed by treatment of the mixture with hot EtOH, in which (I) is sparingly sol. The m.p. of the condensation product with o -C₆H₄Cl·CHO should be determined as a check on the identity of the alcohol. E. C. S.

Nitric oxide and alkyl ethers. M. W. TRAVERS (Nature, 1937, 140, 107).—A discussion of the mechanism of the reaction occurring between Me₂O and NO (cf. A., 1937, I, 366). L. S. T.

Diisothiocyanomethyl and di- α -isothiocyanomethyl ethers. H. R. HENZE, A. J. HILL, and L. B. CROSS (J. Org. Chem., 1937, 2, 29—35).—KSCN (4.1) and (CH₂Cl)₂O (1 mol.) in dry C₆H₆ at 110° give 88% of *diisothiocyanomethyl ether*, b.p. 101.5—102°/2.5—3 mm., m.p. 18.5°, hydrolysed by H₂O to CH₂O and HNCS, and giving with NH₃·Et₂O *dithiocarbamidomethyl ether*, b.p. 147—149° (corr.), and with NH₂Ph or *o*-C₆H₄Me·NH₂ in dry C₆H₆ *di-phenyl*, m.p. 159.5°, and *o-tolyl-thiocarbamidomethyl ether*, m.p. 169—169.5°, respectively; the two last-mentioned ethers with hot EtOH yield *N-ethoxyethyl-N'-phenyl*, m.p. 135—136°, and *o-tolyl-thiocarbamide*, m.p. 127.5—128.5°, respectively. (CHMeCl)₂O with NaSCN (not KSCN) in C₆H₆ at 110° gives *di- α -isothiocyanoethyl ether* (I), b.p. 94.5°/2—3 mm., m.p. -7°, converted by NH₃·Et₂O into "diethylidenethiocarbamide," NH<CHMe·NH>CS, m.p. 182—183.5° (*picrate*, m.p. 241—245°), and by NH₂Ph or *o*-C₆H₄Me·NH₂ into *phenyl*- and *o-tolyl-thiocarbamide*, respectively. The reactions of (I) involve fission of the O linking. Both (SCN)₂-ethers are vesicants, unstable to O₂ and H₂O. R. S. C.

Thermal decomposition of ethylene oxide.—See A., I, 466.

Homologues of ethylene oxide and ethane- α -diol; mechanism of formation of chlorohydrins. H. MOUREU and M. DODÉ (Bull. Soc. chim., 1937, [v], 4, 281—295).—The rates of the reactions of Cl₂·H₂O with C₂H₄, C₃H₆, CH₂Et·CH₂, and CMe₂·CH₂ with formation of the chlorohydrin are comparable with one another, but that with (·CHMe)₂ is much slower. This is considered to support the view that polarisation of the ethylene precedes the reaction and possibly determines its rate. The mechanism proposed by Frahm (A., 1931, 598) involving (CH₂)₂O as an intermediate in the formation of epichlorohydrin (I) does not hold, since, under the conditions of experiment, the rate of reaction between HCl and (CH₂)₂O is much slower than that between Cl₂, H₂O, and C₂H₄, and the ratio of Cl appearing as HCl to the

total Cl appearing as (I) and HCl remains const. and ~0.5, as required by Cl₂ + H₂O + C₂H₄ = CH₂Cl·CH₂·OH + HCl. The above-mentioned ethylenes are best converted into the corresponding glycols through the chlorohydrins, which with boiling Ca(OH)₂·H₂O give the corresponding oxides. These being very volatile are readily separated, and are then hydrated to the glycol (cf. A., 1935, 63).

H. G. M.

Preparation of α -dichaulmoogroylglycerol- β -phosphoric acid. T. WAGNER-JAUREGG and H. ARNOLD (Ber., 1937, 70, [B], 1459—1462).—The acids obtained by hydrolysis of chaulmoogra oil and hence probably containing hydnocarpic acid are converted into the *Na*, m.p. 225° after softening at 210°, and *Pb*, m.p. 62—63°, salts, which with OH·CH(CH₂Br)₂ in boiling xylene yield *α -dichaulmoogrin*, m.p. 47—48°. This is converted by the successive action of POCl₃ in C₂H₅N and ice into *α -dichaulmoogroylglycerol- β -phosphoric acid* (*Pb*, m.p. 175° after softening at 155°, *choline*, m.p. 160—165° after softening at 60°, and *Na*, m.p. 149—150°, salts).

H. W.

Catalytic toxicity and chemical structure. II. Influence of chain length in the alkyl sulphide and thiol series.—See A., I, 418.

Structure of dihalogeno-dialkyl sulphides and selenides, and of their complexes with auric chloride and platonic bromide. P. SPINOGLIO (Gazzetta, 1937, 67, 318—324).—SMe₂Br₂ presumably has the structure [SMe₂Br]⁺Br⁻, since it forms compounds formulated as [SMe₂Br]⁺AuCl₃Br⁻ and [SMe₂Br]₂⁺PtBr₆⁻ (I). [SeMe₂Br]⁺Br⁻ similarly gives a compound, [SeMe₂Br]₂⁺PtBr₆⁻ (II). When (I) and (II) are washed with boiling H₂O, compounds, [SMe₂]₂PtBr₄ and [SeMe₂]₂PtBr₄, are obtained.

E. W. W.

Methylenedisulphonic acid and its derivatives. J. C. BAUER and G. L. JENKINS (J. Amer. Pharm. Assoc., 1937, 26, 485—493).—Modifications of the methods of Schroeter (A., 1905, i, 851; 1919, i, 516; 1928, 1216) for the prep. of CH₂(SO₃H)₂ are suggested. Attempts to prepare its cyclic ureide failed.

F. O. H.

Constitution of formic acid. K. M. PANDALAI (J. Indian Chem. Soc., 1937, 14, 172—175).—Biochemical evidence indicates that the activated acid is :C(OH)₂. It follows that the ordinary acid is HCO₂H.

F. J. G.

Hydrolysis of esters and the Knoevenagel reaction.—See A., I, 417.

Enzymic dehydrogenation of trideuteroacetic acid. R. SONDERHOFF and H. THOMAS (Annalen, 1937, 530, 195—213; cf. A., 1936, 1418).—The aerobic reaction of CD₃·CO₂Na is only slightly < that of NaOAc with yeast and (·CD₂·CO₂Na)₂ is dehydrogenated almost as readily as (·CH₂·CO₂Na)₂ in presence of an enzyme material from the horse heart. Dehydrogenation of CD₃·CO₂Na with 86 mol.-% of D gave (·CD₂·CO₂Na)₂ with 40.6 mol.-%. Similarly (CD₃·CO₂)₂Ba yielded citric acid (I) with 55.8 at.-% D. During the action cell material is formed by the yeast. Extraction of the latter with light petroleum yields a fat with 23% D and the

residue yields to Et_2O an acid fat with 23% D. There remains a carbohydrate with 1.6 mol.-% D which consequently cannot be the source of (I). The unsaponifiable matter of the fat contains 31.0% D. It appears therefore that both intermediate products of the degradation and the materials formed by the use of $\text{CD}_3\text{CO}_2\text{Na}$ as substrate have a considerable content of non-exchangeable D and also that unforeseen losses of D occur. It is possible to use D as indicator in investigating the fate of org. mols. or portions thereof but conclusions as to the course of the change can only be very cautiously drawn.

H. W.

Thermal and photochemical decomposition of acetyl peroxide.—See A., I, 471.

Esters of castor oil fatty acids. I—IV. Y. TOYAMA and T. ISHIKAWA (J. Soc. Chem. Ind. Japan, 1937, 40, 172—174B).—The esters of ricinoleic, polyricinoleic (I), and oleic acids with glycerol, $(\text{CH}_2\text{OH})_2$, MeOH, EtOH, BuOH, *iso*- $\text{C}_5\text{H}_{11}\text{OH}$, cyclohexanol, and methylcyclohexanol have been prepared and their viscosities and m.p. are discussed. The influence of small quantities of these esters on the m.p. and η of castor oil is discussed. The esterification of (I) with the Me and Et esters of (I) is described and acid vals. and η of the products are discussed.

J. D. R.

Synthesis of stearic acid. R. KUHN, C. GRUNDMANN, and H. TRISCHMANN (Z. physiol. Chem., 1937, 248, IV—V).—Piperidine (I) salts with crotonaldehyde yield octatrienal, dodecapentaenal, and hexadecapentaenal (II), m.p. 217—218° (decomp.). (II) with $\text{CH}_2(\text{CO}_2\text{H})_2$ and (I) gives *heptadecapentaene- α , α -dicarboxylic acid*, which in AcOH with $\text{PtO}_2\text{--H}_2$ followed by distillation/0.0003 mm. gives stearic acid. Catalytic hydrogenation of (II) gives cetyl alcohol.

W. McC.

Conjugated dehydrogenation of ricinoleic acid. M. P. BELOPOLSKI and O. B. MAXIMOV (Maslob. Shir. Delo., 1937, No. 2, 13—14).— λ -Keto-stearic acid is obtained by heating castor oil at 250° with Ni, Cu (1 hr.; 40% yield), or Pd (30 min.; 60% yield).

R. T.

Syntheses from castor oil. II. C. H. KAO and W. S. CHANG (Sci. Rep. Nat. Tsing Hua Univ., 1937, 4, A, 35—39; cf. A., 1934, 753).—Octan- β -ol (I) is best (95%) obtained from castor oil by H_2SO_4 at 140°; it and *n*- $\text{C}_8\text{H}_{17}\text{OH}$ at 400—450° give an octene, b.p. 94—95°, and heptene, b.p. 121—122° (*n* and *d* given), and are hydrogenated to C_8H_{18} and C_7H_{16} , respectively. PBr_3 and (I) give $\text{C}_8\text{H}_{17}\text{Br}$ and thence (Cu—Zn) C_8H_{18} in 82% overall yield. A 66% yield of heptic acid is obtained from (I) by $\text{Na}_2\text{Cr}_2\text{O}_7$.

R. S. C.

Ethyl orthohalogenoacetates and their reaction with zinc and magnesium. F. BEYERSTEDT and S. M. McELVAIN (J. Amer. Chem. Soc., 1937, 59, 1273—1275).—*Et chloro-orthoacetate*, $\text{CH}_2\text{Cl}\cdot\text{C}(\text{OEt})_3$, b.p. 74—75°/13 mm., from $\text{CH}_2\text{Cl}\cdot\text{CN}$ via $\text{CH}_2\text{Cl}\cdot\text{C}(\text{OEt})\cdot\text{NH}_2\cdot\text{HCl}$ (Sah, A., 1928, 394), does not react with Zn or Mg. The *bromo-orthoacetate*, b.p. 77—79°/9 mm., prepared (together with a trace of Br_2 -compound, b.p. 102—104°/8 mm.) by brominating $\text{CMe}(\text{OEt})_3$ in $\text{C}_5\text{H}_5\text{N}$ at 10°, when heated with Zn or

Mg in Bu_2O gives organometallic bromides which further yield non-volatile products by intermol. condensation. The iodo-orthoacetate (from the Br-compound by heating with NaI—EtOH in sealed tubes at 110° for 16 hr.) reacts similarly but more readily.

A. Li.

Abnormal acetoacetic ester synthesis. I. Reaction of sodium with allyl, benzhydryl, and cinnamyl acetate. H. F. TSEOU and Y. T. WANG (J. Chinese Chem. Soc., 1937, 5, 224—229).—In accordance with the author's electronic view of the acetoacetic ester synthesis, the action of Na on allyl acetate gives allyl Δ^2 -pentenoate whilst *benzhydryl acetate*, b.p. 152—153°/1 mm., m.p. 13°, and *cinnamyl acetate*, b.p. 114°/1 mm., afford $\text{CHPh}_2\cdot\text{CHPh}_2$ and α , α -diphenyl- Δ^2 -hexadiene with its dimeride, respectively.

H. W.

Mechanism of oxidative processes. XLVII. Induced reactions, particularly the "activation" of oxalic acid. H. WIELAND and W. ZILG (Annalen, 1937, 530, 257—273).—The activation of $\text{H}_2\text{C}_2\text{O}_4$ is caused by the reception of energy from the primary process of oxidation. The dehydrogenated residue of $\text{H}_2\text{C}_2\text{O}_4$, either C_2O_4 or CO_2 , transmits a portion of the energy liberated during the oxidation to other $\text{H}_2\text{C}_2\text{O}_4$ mols. which thus become activated. If the loosened, reactive H finds a suitable acceptor (HgCl_2 or O_2) further transference of energy occurs with production of a reaction chain. Contrary to Oberhauser and Hensinger the formation of H_2O_2 when O_2 is bubbled through solutions in which $\text{H}_2\text{C}_2\text{O}_4$ has been partly oxidised by a deficiency of KMnO_4 is not due to the persistence of activated $\text{H}_2\text{C}_2\text{O}_4$ mols. since a similar behaviour is exhibited by solutions containing MnC_2O_4 and $\text{H}_2\text{C}_2\text{O}_4$ but not by $\text{H}_2\text{C}_2\text{O}_4$ or Mn^{II} salt and O_2 ; the production of HCO_2H or other volatile acid could not be detected. The reaction between $\text{H}_2\text{C}_2\text{O}_4$, Fe^{II} , and H_2O_2 is very sensitive to light; with excess of H_2O_2 reaction ceases when all Fe^{II} has been oxidised to Fe^{III} . The initial impulse follows very rapidly in light and in the dark. More CO_2 is formed in the light, the difference being due to a photochemical decomp. of $\text{H}_2\text{C}_2\text{O}_4$ comparable with Eder's reaction. In the reaction between $\text{H}_2\text{C}_2\text{O}_4$ activated by $\text{Fe}^{II}\text{--H}_2\text{O}_2$ and HgCl_2 , CO_2 and HgCl are produced in equiv. amounts. Dehydrogenation of $\text{H}_2\text{C}_2\text{O}_4$ occurs almost exclusively through the HgCl_2 ; Fe^{II} and H_2O_2 are involved only so far as is necessitated by the primary activation of $\text{H}_2\text{C}_2\text{O}_4$. If the reaction occurs in light, the Eder reaction which causes increase in the pptd. HgCl is accompanied by the dehydrogenation of $\text{H}_2\text{C}_2\text{O}_4$ by H_2O_2 in light. The incidence of the latter change is betrayed by the gradual disappearance of H_2O_2 and by the excess of CO_2 produced above the ratio $\text{CO}_2 : \text{HgCl} : : 1 : 1$. The reaction $\text{H}_2\text{C}_2\text{O}_4\text{--Fe}^{II}\text{--H}_2\text{O}_2\text{--HgCl}_2$ is somewhat restricted by pyrogallol, resorcinol, and most appreciably by quinol but little by HCN. In the dark $\text{H}_2\text{C}_2\text{O}_4$ cannot be replaced by $\text{CH}_2(\text{CO}_2\text{H})_2$, $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, tartaric acid, malic acid, or HCO_2H whereas a slight pptn. of HgCl occurs in the light with all acids except $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$. The induction impulse, characteristic of $\text{H}_2\text{C}_2\text{O}_4$, is observed to a very slight degree only with HCO_2H and

in light. HCO_2H causes a slow separation of HgCl in amount dependent on the time of illumination; the HCO_2H is oxidised by H_2O_2 , activated by Fe^{++} . Replacement of Fe^{++} by Co or Ni gives formation of HgCl in the dark and of rather more thereof in the light. Fe^{+++} is inactive in the dark. In the light Mn^{++} behaves similarly to Fe^{++} . Et_2O_2 , $\text{OBz}\cdot\text{O}\cdot\text{SO}_3\text{K}$ and Bz_2O_2 resemble H_2O_2 in their action whereas O_3 is ineffective. The activating effect of $\text{K}_2\text{S}_2\text{O}_8$ is described in detail, with the effect thereon of the acidity of the solution.

Maleic acid is quantitatively converted into fumaric acid when boiled with aq. HgCl_2 and a trace of $\text{K}_2\text{S}_2\text{O}_8$; the change occurs more slowly without HgCl_2 . The conversions, citraconic to itaconic acid, *allocinnamic* to cinnamic acid, oleic to elaidic acid are effected similarly. The changes are ascribed to an inductive impulse which acquires its energy from a primary, slight oxidation. Small amounts of $\text{K}_2\text{S}_2\text{O}_8$ are consumed in the change.

H. W.

Preparation of malonic ester. C. H. KAO and K. H. CHEN (J. Chinese Chem. Soc., 1937, 5, 223).—Finely divided $\text{CH}_2(\text{CO}_2)_2\text{Ca}$ suspended in 95% EtOH is treated with HCl ; after addition of C_6H_6 or CCl_4 the mixture is boiled for 3 hr. and the $\text{CH}_2(\text{CO}_2\text{Et})_2$ is isolated as usual. The yield is about 70% calc. on the $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ used.

H. W.

Halogenometric determination of fumaric acid in presence of those accompanying compounds common in biochemistry. E. SZEGEDY (Z. anal. Chem., 1937, 109, 316—333).—Fumaric acid, in the presence of succinic, *l*-malic, pyruvic, oxalacetic, malonic, and arsenious acids, H_2SO_4 , and phosphate buffer mixture, is separated as Hg fumarate (I) by pptn. with $\text{Hg}_2(\text{NO}_3)_2$ from solutions containing 5% of free HNO_3 . (I) may be weighed as such or, better, is converted into Na fumarate by boiling with NaCl or NaOH , and is then determined bromometrically. WO_4^{--} , if present, is first separated by pptg. WO_3 with H_2SO_4 .

J. S. A.

Determination of tartaric acid as lead tartrate. C. H. MANLEY (Analyst, 1937, 62, 526—530).—The Pb salt is pptd. by addition of $\text{Pb}(\text{NO}_3)_2$ to a solution of the tartrate previously made neutral to phenolphthalein.

E. C. S.

Use of the name "racemic acid." A. FINDLAY (Nature, 1937, 140, 22).—Historical.

L. S. T.

Thermal decomposition of $\alpha\alpha'$ -diethoxydicarboxylic acids. M. MEYER (Compt. rend., 1937, 204, 1948—1949; cf. A., 1937, II, 246).— $\alpha\alpha'$ -Diethoxypimelic acid when distilled at 760 mm. gives traces of aldehyde. $\alpha\alpha'$ -Diethoxysuberic acid, treated similarly, gives Δ^1 -cyclopentene-1-aldehyde, b.p. $60\text{--}65^\circ/15$ mm. [semicarbazone, m.p. 222° (block) (lit., 208—209°)], and $\alpha\alpha'$ -diethoxytetradecanedicarboxylic acid gives decane- $\alpha\alpha$ -dialdehyde, b.p. $128\text{--}130^\circ/4$ mm. (semicarbazone, m.p. 202°).

J. L. D.

Reactions of ascorbic acid. G. WOKER and I. ANTENER (Helv. Chim. Acta, 1937, 20, 732—741).—The determination of ascorbic acid (I) by reduction of picric acid-picric acid also involves glutathione, cysteine (II), and creatinine (III); the iodate reduction method

is more advantageous since it involves only acid reducing reagents. The blue colour with benzoquinone is given much more rapidly by (I) than by (II), whilst (III), xanthine, and uric acid are inactive. The conversion of (I) into furfuraldehyde and its treatment with orcinol or phloroglucinol are practicable but not very sensitive by reason of the discoloration of the controls by HCl alone. The reaction of (I) with $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$ or thymol and the osazone reaction of dehydroascorbic acid are described.

H. W.

Determination of total and of reduced ascorbic acid with methylene-blue.—See A., III, 327.

Production of peroxide during the auto-oxidation of ascorbic acid and of thiol compounds. P. HOLTZ and G. TRIEM (Z. physiol. Chem., 1937, 248, 1—4; cf. Langenbeck, this vol., 167).—When O_2 is passed through a mixture of ascorbic acid (I) with a dil. solution of luminol in aq. Na_2CO_3 containing a trace of haemin strong luminescence, not affected by addition of Cu^{++} , is observed. Weaker luminescence, strengthened by Cu^{++} , is observed when (I) is replaced by cysteine (II) or thiolacetic acid (III). (I) is much more rapidly oxidised than are (II) and (III), the increase in rate of oxidation produced by Cu^{++} being insufficient to affect the strength of luminescence. Cu^{++} very greatly increases the rate of oxidation of (II) and (III). Distillates from the mixtures contain H_2O_2 derived, presumably, from the labile org. peroxides produced by the oxidation.

W. McC.

Preparation and properties of the osazone of dehydroascorbic acid. I. ANTENER (Helv. Chim. Acta, 1937, 20, 742—746).—Air oxidation of ascorbic acid affords dehydroascorbic acid, isolated as the osazone, m.p. 218° . The absorption spectrum shows max. at 196, 266, 348, and 441 μ .

P. G. C.

Structure of pectin polygalacturonic acid. P. A. LEVENE and L. C. KREIDER (Science, 1937, 85, 610).—Degradation of the acid with HIO_4 yields *l*-tartaric acid. $\text{C}_{(4)}$ and $\text{C}_{(5)}$ are therefore engaged in the ring formation and in the condensation of each unit with its neighbouring unit. It is predicted that the OH of $\text{C}_{(4)}$ serves for condensation and that of $\text{C}_{(5)}$ for ring formation.

L. S. T.

Photopolymerisation of formaldehyde to reducing sugars *in vitro*. A. RAM and N. R. DHAR (J. Indian Chem. Soc., 1937, 14, 151—155).—Small yields of reducing sugars are obtained when aq. CH_2O in presence of FeCl_3 is exposed to sunlight. The yield is increased in presence of kieselguhr and is a max. at $30\text{--}40^\circ$.

F. J. G.

Relation between velocity of the Cannizzaro reaction and the concentration of aldehyde. I. CANNIZZARO reaction in formaldehyde solutions. E. K. NIKITIN and I. I. PAUL (J. Gen. Chem. Russ., 1937, 7, 1292—1298).—Aq. CH_2O is determined as follows: 10 ml. of solution or H_2O are heated at $50\text{--}60^\circ$ for 30—40 min. with 10 ml. of 50% KOH , the vol. is made up to 100 ml., and 10 ml. of each solution are titrated with 0.15N- H_2SO_4 ; the $[\text{CH}_2\text{O}] \propto$ difference between the two titrations. The velocity of the Cannizzaro reaction $\propto [\text{CH}_2\text{O}]$ and temp.

R. T.

Direct method for the differentiation of acetals from ethers. H. F. TSEOU and T. S. CHOW (J. Chinese Chem. Soc., 1937, 5, 179—185).—The acetal (4 drops) is added to 0.5 c.c. of a solution of resorcinol, α - or β -C₁₀H₇·OH, or PhOH in EtOH and 1 c.c. of aq. H₂SO₄ (1 : 4) is slowly introduced down the side of the tube. A colour, usually red, is produced at the junction of the two layers. On shaking the mixture a coloured ppt. is formed which further changes in colour on addition of NaOH or NH₃. Results with the following acetals are tabulated: CH₂(OMe)₂, CH₂(OEt)₂, CHMe(OMe)₂, CHMe(OEt)₂, CHMe(OPrⁱ)₂, CHMe(Obuⁱ)₂, CHPrⁱ(OPrⁱ)₂, CHPrⁱ(O·C₅H₁₁)₂, CHPrⁱ(OMe)₂, CHPrⁱ(OEt)₂, CHPrⁱ(Obuⁱ)₂, CHPh(OMe)₂, CHPh(OEt)₂. Ethers do not give the reaction. H. W.

Kinetics of polymeric aldehydes. V. Polyoxyethylene dihydrates.—See A., I, 468.

Organic catalysts. XVII. Hydration of crotonaldehyde to aldol. W. LANGENBECK and R. SAUERBIER (Ber., 1937, 70, [B], 1540—1541).—Crotonaldehyde (I) is partly converted into aldol (II) when heated at 40° in aq. AcOH or EtOH containing sarcosine (III) or piperidine but not glycine. The change does not occur in absence of a catalyst. (II) is partly dehydrated to (I) when kept at 40° in aq. AcOH containing (III). H. W.

Mobility of halogens in $\alpha\beta$ -dichlorocarbonyl derivatives. M. NAFTALI (Bull. Soc. chim., 1937, [v], 4, 333—342).—Acetals of $\alpha\beta$ -dichloro-aldehydes with an α -H are converted by alkali alkoxides into the acetals of α -chloro-unsaturated aldehydes, but little or no reaction occurs, even in hot conc. solution, when the α -H has been replaced by alkyl. Thus CH₂Cl·CHCl·CH(OMe)₂, b.p. 78—82°/13 mm. (cf. lit.; prep. described), when treated with excess of NaOMe-MeOH (water-bath; 1 hr.) gives α -chloro- Δ^a -propenal Me₂ acetal, b.p. 28°/12 mm., and similarly $\alpha\beta$ -dichlorobutanal Me₂ acetal, b.p. 86—90°/13 mm., prepared from the aldehyde and MeOH in presence of 1% of HCl (4 hr. at the b.p.), gives α -chloro- Δ^a -butenal Me₂ acetal, b.p. 58°/13 mm. $\alpha\beta$ -Dichloro- α -methylbutanal Me₂, b.p. 88°/13 mm., and Et₂, b.p. 98—100°/12 mm., acetal, and $\alpha\beta$ -dichloro- α -methylhexanal Me₂, b.p. 118°/13 mm., and Et₂, b.p. 127°/11 mm., acetal (preps. described) are very stable towards NaOMe, and even when boiled with conc. NaOMe-MeOH for 3 days give only small fractions of a composition close to that of the corresponding monochloride. CMe₂Br·CH(OMe)₂, b.p. 54—55°/13 mm. (cf. A., 1910, i, 92), is unaffected when heated (water-bath) with 10, 20, and 30% aq. KOH during 8 hr., or during 3 hr. with KOH-EtOH, or with powdered KOH, but with powdered KOH at 120—140° a poor yield of CH₂:CMe·CH(OMe)₂ is obtained. CH₂Cl·CHClAc, b.p. 65—70°/16 mm., resinifies when treated with NaOMe-MeOH. Addition of Cl to CHMe:CMeAc in CHCl₃ gives Me $\alpha\beta$ -dichloro- α -methylpropyl ketone, b.p. 66°/13 mm., and a compound, b.p. 96—99°/13 mm., probably Me $\alpha\beta\gamma$ -trichloro- α -methylpropyl ketone. The former, like the Cl-additive product of mesityl oxide, when treated with NaOMe-MeOH gives a mixture probably consisting chiefly of an unsaturated mono-ether. H. G. M.

Constitution and properties of dichloro- and dialkoxy-aldehydes. J. LICHTENBERGER and M. NAFTALI (Bull. Soc. chim., 1937, [v], 4, 325—333).—The following have been prepared by addition of Cl to the appropriate unsaturated aldehyde in CHCl₃ or CCl₄: $\alpha\beta$ -dichloro- α -methylbutanal (I), b.p. 52—53°/12 mm., $\alpha\beta$ -dichloro- α -methylpentanal (II), b.p. 67°/13 mm., and $\alpha\beta$ -dichloro- α -ethylhexanal. The last two when treated with cold NaOAlk in excess of AlkOH give the corresponding $\alpha\beta$ -alkoxy-compounds in good yield: $\alpha\beta$ -dimethoxy- (III), b.p. 67°/12 mm., -diethoxy-, b.p. 81°/12 mm., and -di-n-propoxy-, b.p. 104°/12 mm., - α -methylpentanal; $\alpha\beta$ -dimethoxy-, b.p. 87°/13 mm., -diethoxy-, b.p. 87—88°/4 mm., -di-n-propoxy-, b.p. 97°/3 mm., and -di-n-butoxy-, decomp. at about 70—80°/1 mm., α -ethylhexanal. (I) and its lower homologues when similarly treated with NaOAlk-AlkOH are completely decomposed and resinified. Mono-ethers corresponding with the above di-ethers cannot be obtained with half the quantities of NaOAlk previously used; there does not appear to be any difference in the mobility of the two Cl. Attempts to oxidise the foregoing dialkoxy-aldehydes to the corresponding acids, to reduce them to the corresponding alcohols, and to prepare solid derivatives (by means of NaHSO₃, NPh·NH₂, p-NO₂·C₆H₄·NH·NH₂, NH₂·CO·NH·NH₂·HCl, and NH₂OH) from them failed; and qual. tests for ·CHO gave positive indications only after some hr. The corresponding chloro-aldehydes are also unreactive. The possibility of an alternative, cyclosemiactal structure

CHMeX< $\begin{smallmatrix} \text{CHEt} \\ \text{CHX} \end{smallmatrix}$ >O (X = Cl, OMe) for (II) and (III), respectively, is discussed. Oxidation of α -ethyl- β -n-propylacetaldehyde with moist Ag₂O yields α -ethyl- Δ^a -hexenoic acid, b.p. 107—108°/3 mm., which with Cl₂-CHCl₃ gives $\alpha\beta$ -dichloro- α -ethylhexoic acid, b.p. 134°/3 mm., resinified by NaOMe. H. G. M.

Photo-decomposition of aldehydes and ketones.—See A., I, 471.

Accelerating action of ketones on the Cannizzaro-Tischtschenko reaction. I. M. N. TLIT-SCHENKO (J. Gen. Chem. Russ., 1937, 7, 1086—1092).—The activity of a no. of ketones in accelerating the Cannizzaro reaction of 10% CH₂O with 0.1N-KOH \propto ketone concn., and inversely \propto [H₂O], and rises in the order pinacolin < valerone < COPr₂ < COMePr < COPhEt < COMe₂ < COEt₂ < COMeEt < COPhMe < cyclohexanone. This order is, however, different for different [CH₂O]. R. T.

Determination of acetone by the reaction with salicylaldehyde. E. K. NIKITIN and S. A. VERSCHINSKI (J. Appl. Chem. Russ., 1937, 10, 755—758).—1 ml. of 50% KOH and 0.5 ml. of 5% salicylaldehyde in EtOH are heated at 50° for 25 min. with 1 ml. of the solution (containing $\pm 0.001\%$ COMe₂), and with 1 ml. of standard aq. COMe₂ (0.002—0.01%). 1 ml. portions of the resulting solutions are added to 10 ml. of 60% H₂SO₄, and the colorations are compared. The max. mean error is $\pm 2\%$. R. T.

Glucufuranosides and thioglucufuranosides. I. Method of preparation and its application to galactose and glucose. J. W. GREEN and E.

PACSU (J. Amer. Chem. Soc., 1937, **59**, 1205—1210).—Glucose alkyl (Et or CH₂Ph) mercaptals are converted by HgCl₂ in EtOH at 20° into α -ethylglucopyranoside, but under neutral conditions (excess of HgO) yield the ($\alpha + \beta$) ethyl- (excess of HgCl₂) or α -alkylthio- (1 mol. of HgCl₂) -glucofuranosides. Hudson's rules, ready hydrolysis, and conversion by HgCl₂ (HgO) into the ethylfuranoside indicate that the latter is furanoid (cf. Schneider, A., 1916, i, 792; 1918, i, 252); HCl-EtOH converts β -ethylgalactoside or ($\alpha + \beta$)-ethylgluco-furanoside into the ($\alpha + \beta$)-pyranoside. With galactose, the intermediate thio-galactofuranoside cannot be isolated. A. LI.

Factors influencing the destruction of glucose and fructose by oxygen. M. CLINTON, jun., and R. S. HUBBARD (J. Biol. Chem., 1937, **119**, 467—472).—39.5% destruction of fructose occurs in PO₄''' buffer solutions at p_H 7.0 and 77.5° in presence of O₂, whilst only 5.7% of glucose is similarly destroyed. No destruction occurs in either case if O₂ is replaced by N₂. Only with PO₄''' and AsO₄''' buffers does destruction of fructose occur. Purification of the reagents shows that such destruction is catalysed by some unknown impurity. No hexose phosphate esters could be isolated. P. G. M.

Analysis of fructoside mixtures by means of invertase. VI. Methylated and acetylated derivatives of crystalline β -benzylfructopyranoside. C. B. PURVES and C. S. HUDSON (J. Amer. Chem. Soc., 1937, **59**, 1170—1174).—CH₂Ph·OH-HCl slowly converts α -methyl- or α -benzyl-fructofuranoside into β -benzylfructopyranoside (I), m.p. 157°, [α]_D²⁰ -130° in H₂O, acetylation of which with specially purified C₅H₅N and Ac₂O gives the *tetra-acetate*, m.p. 69—69.5°, [α]_D²⁵ -128.4° in MeOH, whilst treatment with TIOEt followed by methylation yields the *Me₂ ether* (liquid), [α]_D²⁰ -114° in dioxan, and further methylation the *Me₄ ether*, [α]_D²⁰ -111.8° in dioxan. (I) is best prepared (30% yield) by shaking fructose with CH₂Ph·OH-HCl, evaporating, extracting with C₆H₆, and crystallising from H₂O; the C₆H₆ extract, after fermentation and acetylation, yields the *tetra-acetyl- α -benzylfuranoside* (5%). The rates of hydrolysis of (I) and β -methylfructopyranoside [prepared by the action of MeOH-HCl on (I)] with HCl are respectively 1.3 and 0.8 times that of sucrose. A. LI.

Direct demonstration of the sucrose linking in the oligosaccharides. H. W. RAYBIN (J. Amer. Chem. Soc., 1937, **59**, 1402—1403).—Gentianose and stachyose give the blue-green colour with diazouracil, characteristic of the sucrose linking (Raybin, A., 1933, 811). A. LI.

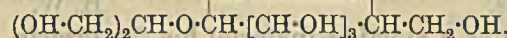
Fructose anhydrides. XVIII. **Constitution of tritacin.** H. H. SCHLUBACH and H. PEITZNER (Annalen, 1937, **530**, 120—130; cf. A., 1936, 1096).—By a modified purification involving repeated fractional pptn., tritacin (I) is obtained non-hygroscopic, colourless, and almost tasteless, with [α]_D²⁰ -51.4° in H₂O and mol. wt. (cryoscopy in H₂O) 2600—2830 (16—17.5 fructose anhydride units). Exhaustive purification of the *Ac* derivative (43.5% *Ac*), [α]_D²⁰ -15.6° in CHCl₃, *forms*, m.p. 115° and 191°, and subsequent hydrolysis gives an identical product.

P** (A., II.)

Quant. hydrolysis indicates that (I) contains only fructose anhydride units. Me₂SO₄-KOH-COME₂ readily gives a *methyltritacin* (45—46% OMe), m.p. 141—151°, [α]_D²⁰ -61.2° in CHCl₃, hydrolysed by H₂C₂O₄ in aq. EtOH to a 3 : 1 : 3 mixture of 1 : 3 : 4 : 6-tetra-, a new *tri-*, b.p. 86°/0.01 mm., [α]_D²⁰ -10.5° → -13.8° in H₂O, +3° → -5.5° in MeOH, and +12.2° → +5.9° in CHCl₃ (*osazone*, m.p. 77.5°), and *dimethylfructose*, b.p. 132—136°/0.1 mm. (probably identical with that obtained from trimethylsinistrin). (I) probably contains a closed ring containing 7 fructose anhydride units repeated regularly. Staudinger's branched-chain formula for starch is rejected.

R. S. C.

Floridoside, a *d*-monogalactoside of glycerol. H. COLIN (Bull. Soc. chim., 1937, [v], 4, 277—281; cf. A., 1934, 121).—Floridoside, C₉H₁₈O₈·H₂O, m.p. 86—87°, [α]_D²⁰ +151° in H₂O (optical and crystallographic data given), is hydrolysed to glycerol and galactose by acids, and also by the common moulds and bottom yeast, but not by invertase and emulsin. It is oxidised with difficulty by Br-H₂O and unaffected by acetobacteria capable of converting glycerol into dihydroxyacetone. It is therefore considered to be β -(α -*d*-galactosido)glycerol,



H. G. M.

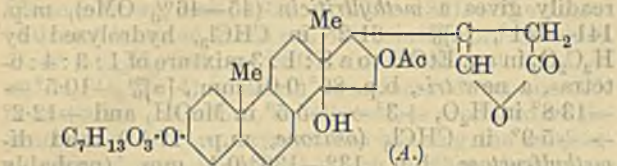
Ericolin. H. DIETERLE and O. DORNER (Arch. Pharm., 1937, **275**, 380—382).—Ericolin, from the leaves of *Arctophylos uva ursi*, is shown by hydrolysis to quinol and glucose and by purification to be impure arbutin. R. S. C.

Vegetable heart poisons. XV. **Oleandrin.** R. TSCHESCHE (Ber., 1937, **70**, [B], 1554—1556).—The identity of folinerin with oleandrin is established. Cautious oxidation of oleandrin (I) with CrO₂ affords *oleandrigenone*, m.p. 250—252°, converted by cold, conc. H₂SO₄ into a dianhydro-oleandrigenone identical with dianhydrogitoxigenone (digitaligenone). This is possible only if OH at C₍₃₎ in (I) was free and has become oxidised to CO. *Ac* must therefore be attached to C₍₁₆₎ and the sugar, oleandrose, as in other heart glucosides is united through O to C₍₃₎.

H. W.

Glucosides of the oleander. W. NEUMANN (Ber., 1937, **70**, [B], 1547—1554).—Oleandrin (I), m.p. 250° [α]_D²⁰ -52.1° in MeOH, is identical with folinerin. It is hydrolysed by 0.1N-HCl in aq. MeOH to oleandrigenin (II), m.p. 223° after melting with decomp. at 110—115° and re-solidifying at 140—150°, [α]_D¹⁸ -8.5° in MeOH (which is identical with acetylgitoxigenin), and *oleandrose* (III), m.p. 68—70°, which at 60°/1 mm. passes into *anhydro-oleandrose*, C₇H₁₂O₃. (III) is probably a *Me* ether of a methyldeoxypentose; the OMe of (I) is proper to the sugar component. (I) is hydrolysed by boiling N-H₂SO₄ to *monoanhydro-oleandrigenin* C₂₅H₃₄O₅, m.p. 262°. Partial hydrolysis of (I) by NaOH yields *deacetyloleandrin*, m.p. 238—240°, [α]_D¹⁸ -24.9° in MeOH, obtained also from oleander leaves; it is hydrolysed by 0.1N-HCl to gitoxigenin (IV), [α]_D¹⁸ +35.2° in MeOH. Similar partial hydrolysis of (II) gives (IV) and AcOH, whilst treatment of (II) with

NaOAc and boiling Ac_2O yields diacetylglitoxigenin; this when partly hydrolysed gives a *monoacetyl-*



glitoxigenin, m.p. 236—238°. (I) is probably therefore A. In addition to the two heart glucosides *oleander* leaves contain the pharmacologically inactive glucoside *adynerin* (?), $\text{C}_{23}\text{H}_{34}\text{O}_4$, m.p. 234° after softening at 228°. It appears to contain only one double linking (in the lactone group). It is hydrolysed by 0.1N-HCl in EtOH- H_2O to *adynerigenin*, $\text{C}_{23}\text{H}_{34}\text{O}_4$ or $\text{C}_{23}\text{H}_{34}\text{O}_4$, m.p. 238—242°, $[\alpha]_D^{25} +18^\circ$ in $\text{C}_6\text{H}_5\text{N}$. H. W.

Araban of wheat flour.—See A., III, 332.

Fermentability of dextrans. *Amylohexaose* and different yeast species. H. HAEHN, M. GLAUBITZ, and W. GROSS (Ber., 1937, 70, [B], 1492—1495).—*Amylohexaose* is not fermented by several species of yeast and it is therefore improbable that the larger dextrin mol. is attacked under similar conditions. H. W.

Starch as a starting material for the preparation of succinic acid and bromoform. C. H. KAO, H. C. MOU, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1937, 4, A, 27—29).—1 kg. of starch gives 128 g. of lactic acid and thence by NaOBr 62 g. of CHBr_3 and 40 g. of $(\text{CH}_2\text{CO}_2\text{H})_2$. R. S. C.

Plant colloids. XLIV. Soluble starch from amyloses. M. SAMEC (Kolloid-Beih., 1937, 46, 134—142; cf. A., 1932, 338).—Processes which result in the formation of sol. starch from native starch have been applied to the amyloses obtained by electro-dialysis from potato starch. The resulting products are sol. in hot H_2O only when prepared by methods leading to mol. degradation, and in no case are the solutions stable when cold. An explanation is offered. F. L. U.

Aminated cellulose and starch. F. PANCIOLOTTI (Boll. R. Staz. Sperim. Ind. Carta, 1937, 32, 314—316).—Alkali-cellulose combines with $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ to give *p-nitrobenzylcellulose*, reduced to *p-aminobenzylcellulose*. This can be diazotised and coupled with β -naphthols to give coloured cellulose *azo-ethers*, which retain the ordinary fibrous structure of cellulose. Starch similarly gives *p-nitro-* and *p-amino-benzyl* derivatives, and thence coloured *azo-compounds*; these, however, have lost the adhesive properties of starch. E. W. W.

Methylation of polysaccharides. K. FREUDENBERG and H. BOPPEL (Ber., 1937, 70, [B], 1542).—Ramie or cotton is treated with Me_2SO_4 until it contains 43—44% OMe and then suspended in liquid NH_3 . Na is added, followed after 1.5 hr. by MeI. NH_3 is removed finally at 100°/vac. The methyl-cellulose is pure white, retains the fibrous structure, and is insol. in H_2O in absence of NaI. The loss of viscosity in CHCl_3 is remarkable. The difficulties of micro-determination of OMe are discussed. H. W.

Highly polymerised compounds. CLXV. Osmotic measurements with cellites in glacial acetic acid. H. STAUDINGER and G. V. SCHULZ (Ber., 1937, 70, [B], 1577—1582).—Hess' hypothesis that cellite (I) in very dil. solution in AcOH is degraded to the $(\text{C}_6)_2$ stage is untenable since it does not diffuse through membranes which are permeable to cellobiose octa-acetate and biosan acetate. Osmotic measurements of cellite in AcOH and COMe_2 show that it exists in the same condition in all media and that independently of the concn. the macromols. have mol. wt. 20,000—90,000. Hess' observations are unexplained. H. W.

Highly polymerised compounds. CLXII. Hydrocelluloses. H. STAUDINGER and M. SORKIN (Ber., 1937, 70, [B], 1565—1577).—Cotton wool is treated with 2% NaOH in absence of air and then extracted with EtOH and Et_2O ; it has then degree of polymerisation about 1650. It is treated with various N-acids at $53 \pm 0.5^\circ$ and after defined intervals of time portions are washed free from acid, dried, and their viscosity is determined in Schweitzer's reagent. Degradation takes place much more rapidly with strong than with weak acids, HCl being particularly destructive. The various properties of cellulose as solid do not alter proportionately but only functionally with the degree of polymerisation. No sensible loss in these properties is experienced at a degree 700—800; subsequently diminution is rapid when the degree is <600. Similar observations have been recorded for artificial fibres so that it is not necessary that these should have the same high degree of polymerisation as the natural fibre. The mechanical behaviour is a macromol. property governed by the length of the macromols. and by their arrangement in the solid cellulose. By repeated freezing and thawing cellulose can be dissolved in 10% NaOH or 8% LiOH. Its viscosity is the same in these media and usually about 10—20% > in Schweitzer's reagent, showing that the state of dissolution of the material of degree of polymerisation up to 470 is the same in all three solvents and hence mol. since it is mol. in the last medium. H. W.

Individuality of cellulose micelles.—See A., I, 460.

Chelation of diamines with cupric salts.—See A., I, 420.

Glucosaminol, a reduction product of glucosamine. P. KARRER and J. MEYER (Helv. Chim. Acta, 1937, 20, 626—627).—Glucosamine hydrochloride in H_2O is converted by $\text{H}_2\text{-Ni}$ into *glucosaminol*, m.p. 131—132° (Ac derivative, by hydrogenation of the acetylglucosamine, m.p. 153°, $[\alpha]_D^{25} -11^\circ$ in H_2O), isolated as the *hydrochloride*, m.p. 160—161°. P. G. C.

Configuration of glucosamine. Steric relations between α -amino- and α -hydroxy-acids. P. PFEIFFER and W. CRISTELEIT (Z. physiol. Chem., 1937, 247, 262—268; cf. this vol., 138; Karrer, *ibid.*, 234).—The configuration of *L*-alanine is not altered when NH_2 is replaced by OH (*L*-lactic acid). Curves showing the relation between α and light absorption indicate that the Cu salts of *D*-glucosaminic

acid, *d*-gluconic acid, and *d*-galactonic acid have the same configuration which is that of the antipodes of the natural NH_2 -acids. Hence glucosamine also has this configuration and cannot be regarded as a physiological intermediate between sugars and protein degradation products. W. McC.

Glucoproteins. IV. Determination of hexosamine. J. W. PALMER, E. M. SMYTH, and K. MEYER (J. Biol. Chem., 1937, 119, 491—499).—A modification of Elson and Morgan's method (A., 1934, 175) is the most satisfactory. P. G. M.

Aminoglucoside acetates and their rotatory power. M. FREREJACQUE (Compt. rend., 1937, 204, 1480—1482).—It appears impossible to extend the rules of isorotation to this class of compounds. The following substances are obtained by treating the fully acetylated reducing sugar with the acetate of the requisite base in EtOH, the separation of the mixtures into the α - and β -forms being effected by crystallisation preferably after partial isomerisation by fusion or treatment with acid: α -, m.p. 143° , $[\alpha]_D^{25} +180^\circ$ to $+41.6^\circ$ in CHCl_3 , and β -, m.p. 97° , $[\alpha]_D^{25} -54.8^\circ$ to $+41.6^\circ$ in CHCl_3 , -*anilino*glucose tetra-acetate; α -, m.p. 125° , $[\alpha]_D^{25} +119^\circ$ to $+34.2^\circ$ in CHCl_3 , and β -, m.p. 148° , $[\alpha]_D^{25} -47.6^\circ$ to $+34.2^\circ$ in CHCl_3 , -*p-toluidino*glucose tetra-acetate; α -, m.p. 134° , $[\alpha]_D^{25} +93^\circ$ to $+59.4^\circ$ in CHCl_3 , and β -, m.p. 160° , $[\alpha]_D^{25} -48.8^\circ$ to $+59.4^\circ$ in CHCl_3 , -*p-bromoanilino*glucose tetra-acetate; α -, m.p. 197° , $[\alpha]_D^{25} +101^\circ$ to $+21.2^\circ$ in CHCl_3 , and β -, m.p. 152° , $[\alpha]_D^{25} -31^\circ$ to $+21.2^\circ$ in CHCl_3 , -*anilino*lactose hepta-acetate; α -, m.p. 189° , $[\alpha]_D^{25} +82.3^\circ$ to $+24.8^\circ$ in CHCl_3 , and β -, m.p. 208° , $[\alpha]_D^{25} -29^\circ$ to $+24.8^\circ$ in CHCl_3 , -*p-toluidino*lactose hepta-acetate; α -, m.p. 209° , $[\alpha]_D^{25} +98.3^\circ$ to $+24.7^\circ$ in CHCl_3 , and β -, m.p. 192° , $[\alpha]_D^{25} -14.3^\circ$ to $+24.7^\circ$ in CHCl_3 , -*p-bromoanilino*lactose hepta-acetate; β -*anilino*maltohepta-acetate, m.p. 205° , $[\alpha]_D^{25} +37.5^\circ$ to $+92.5^\circ$ in CHCl_3 ; β -*p-toluidino*maltohepta-acetate, m.p. 182° , $[\alpha]_D^{25} +39^\circ$ to $+94.4^\circ$ in CHCl_3 . H. W.

Absolute configuration of the naturally occurring α -amino-acids. R. C. RAINEY (Nature, 1937, 140, 150).—The probable abs. configuration of these acids has been deduced by the application of Boys' rule to levorotatory β -aminohexane, the configuration of which is the same (this vol., 139). L. S. T.

Combinations of glycine and alanine with mercuric oxide. R. TRUHAUT (Compt. rend., 1937, 204, 1484—1486).—Treatment of glycine with yellow HgO in H_2O gives the unstable compound $(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2\cdot\text{HgO}$ (picrate, $[(\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2\cdot\text{HgO}]_2\cdot\text{C}_6\text{H}_3\text{O}_7\cdot\text{N}_3$), in which NH_2 is determinable by Van Slyke's method but Hg appears partly masked. Similarly, alanine gives the compound, $2\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}\cdot\text{HgO}$. H. W.

Action of ascorbic acid on amino-acids. I. Detection of histidine. II. E. ABDERHALDEN (Fermentforsch., 1937, 15, 285—290, 360—381; cf. A., 1936, 635).—I. Old but not fresh aq. ascorbic acid (I) acquires an orange to red colour on addition of aq. NaOH or KOH. Similar colours appear and NH_3 is slowly liberated when (I) is added to aq. NH_2 -acids (and to related amines, e.g., tyramine), the change

being very rapid and the colour deep in the case of histidine (II). Hence (I) may be used to detect (II).

II. (I) catalyses, in varying degree, the deamination of *d*- and *l*- NH_2 -acids, the action being accelerated by Fe^{II} , Cu, and Mn and by increasing the concn. of (I). The extent of deamination [which is large in the case of (II) only] is affected by $[\text{H}^+]$, temp., and concn. of O_2 . CH_2O is produced on deamination of glycine (III) and MeCHO on that of alanine. Glycine anhydride is also slowly attacked by (I) with liberation of NH_3 . Aq. (III) spontaneously decomposes, especially when very dil., with liberation of NH_3 . The deamination of (III) by adrenaline is inhibited by (I) which prevents production of "omega." W. McC.

β -Hydroxyglutamic acid. E. ABDERHALDEN and H. MURKE (Z. physiol. Chem., 1937, 247, 227—238).—The hydrochloride of the Et_2 ester of β -hydroxyglutamic acid (I) (benzoate), obtained by a modification of the procedure of Harington and Randall (A., 1932, 257), with NaOEt gives the free ester, m.p. 62 — 63° , which, on exposure to light and moisture, changes into the *Et* ester, m.p. 115° , of *hydroxy-pyrrolidinecarboxylic acid*, m.p. 176° . The prep. of the *N*-carbobenzyloxy-, m.p. 159° (strychnine salt; Et_2 ester, b.p. 215 — $225^\circ/2$ — 3 mm.; anhydride, m.p. 132 — 133°), dl- α -bromoisohexoyl, m.p. 158° , and dl-leucyl (II), m.p. 220 — 222° (decomp.) (*Et*₂ ester, m.p. 80 — 82° ; carbobenzyloxy-derivative, m.p. 170°), derivatives of (I) and of the *Et*₂ ester, m.p. 49° , of carbobenzyloxyglutamic acid is described. α -Ketoglutaric acid, obtained from (I) by boiling with conc. HCl, gives a 2:4-dinitrophenylhydrazone, m.p. 214° . The *Et*₂ ester of the diketopiperazine corresponding with (II) has m.p. 202° . W. McC.

Biuret reaction of the pentapeptide tetraglycylglycine. P. E. WENAAS (J. Amer. Chem. Soc., 1937, 59, 1353—1354).—Tetraglycylglycine, when shaken in dil. NaOH with excess of $\text{Cu}(\text{OH})_2$ and the product pptd. with EtOH-Et₂O, yields the pink *Na Cu* salt, $\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_6\text{Na}_3\text{Cu}$, decomp. 279 — 281° . A. Li.

Organic reactions of boron fluoride. XIV.

Reaction of amides with acids and amines. F. J. SOWA and J. A. NIEUWLAND. XV. **Alkylation of benzene with esters.** J. F. McKENNA and F. J. SOWA (J. Amer. Chem. Soc., 1937, 59, 1202—1203, 1204—1205).—XIV. The action of AcOH (or other acid) on the $\text{NH}_2\text{Ac}\cdot\text{BF}_3$ additive compound gives MeCN in 95% yield, and $\text{EtCO}\cdot\text{NH}_2$ yields EtCN. The BF_3 is recovered from the residual $\text{BF}_3\cdot\text{NH}_3$ by conc. H_2SO_4 . Mono- and di-alkyl- and arylalkyl-substituted amides are prepared by boiling the amines with $\text{R}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{BF}_3$.

XV. Mixtures of mono-, di-, and poly-alkylbenzenes are formed by the action of org. or inorg. esters and BF_3 on C_6H_6 ; *n*- and *sec*-Bu esters give *sec*- whilst the *Bu*^t ester gives *tert*-alkylbenzenes, thus showing the intermediate formation of olefines. A. Li.

Phacodyl compounds. R. TIOLLAIS (Bull. Sci. Pharmacol., 1937, 44, 7—35, 164—190).—A review.

Preparation of boron alkyls, B_2R_4 . E. WIBERG and W. RUSCHMANN (Ber., 1937, 70, [B], 1583—1591).—The partly methylated compounds BMeCl_2

and BMe_2Cl , obtained by the action of ZnMe_2 on BCl_3 , are unstable and readily become disproportionated to BMe_3 and BCl_2 . Consequently they are not obtainable from BMe_3 and BeCl_2 . B_2Me_4 could not be isolated as such by the action of BMe_2Cl on Na but the products of its disproportionation B and BMe_3 are obtained.
H. W.

Tetramethylammonium silicate. S. GLIXELLI and T. KROKOWSKI (Rocz. Chem., 1937, 17, 309—313).— SiO_2 gel is dissolved in aq. NMe_4OH at 100° , and the solution is conc. in vac., when NMe_4H meta-silicate, $\text{NMe}_4\text{HSiO}_3 \cdot 8\text{H}_2\text{O}$, m.p. $81\text{--}82^\circ$, separates.
R. T.

Halogeno-organic lead compounds. M. LESBRE (Compt. rend., 1937, 204, 1822—1824; cf. A., 1935, 611).—A nearly saturated solution of CsCl with boiling PbCl_2 in small excess affords $\text{PbCl}_2 \cdot \text{CsCl}$, which when anhyd. gives with EtI , Pr^iI , and Bu^iI in the presence of a little I at room temp. Pb EtI , Pr^i , and Bu^i tri-iodide, decomp. in each case $>90^\circ$, respectively. These give additive compounds, $\text{PbRI}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$, with $\text{C}_5\text{H}_5\text{N}$ and are easily hydrolysed.
J. L. D.

Hydrogenation of acetylenic derivatives. XXVIII. **Dicyclohexenylacetylene and its hydrogenation.** J. S. SALKIND and N. N. SCHVALOV (J. Gen. Chem. Russ., 1937, 7, 1235—1245).—1:1'-Dihydroxydicyclohexylacetylene and KHSO_4 at $145\text{--}155^\circ$ (2 hr.) yield di- Δ^1 -cyclohexenylacetylene (I), b.p. $158\text{--}159^\circ/12$ mm., which with Br gives unidentified products, and with I in CHCl_3 gives a di-iodide, m.p. $172\text{--}173^\circ$. (I) is hydrogenated to $\alpha\beta$ -dicyclohexylethane in presence of Pt, and to $\alpha\Delta^1$ -cyclohexenyl- β -cyclohexylethane, b.p. $136\text{--}137^\circ$, with Pd catalyst.
R. T.

Reaction between inorganic complex compounds and hydrocarbons. G. D. GALPERN (Bull. Acad. Sci. U.R.S.S., 1937, 435—442).— C_6H_6 or PhMe , but not other hydrocarbons, reacts with MX_2 in aq. NH_3 ($\text{M} = \text{Ni}, \text{Co}, \text{Cu}, \text{or Zn}$; $\text{X} = \text{CN or CNS}$), to yield complexes of the type $\text{MX}_2 \cdot \text{C}_6\text{H}_6 \cdot 3\text{NH}_3$. The reaction is reversible, and \approx a fraction of the C_6H_6 is combined. The complexes are decomposed by aq. NH_3 , but quant. regeneration of the C_6H_6 was not achieved. Complexes are not formed when $\text{X}_2 = \text{Cl}_2$ or SO_4 .
R. T.

Formation of benzene in the radiochemical polymerisation of acetylene.—See A., I, 472.

5-Nitroso-m-xylene, m.p. 59° , *o*-, m.p. 61° , and *m*-nitrosoethylbenzene, m.p. 22° ; Pr^s *p*-nitrosobenzoate, m.p. $61\text{--}62^\circ$; *o*-, m.p. 117° , and *m*-iodonitrosobenzene, m.p. 77° ; *m*- and *p*-nitrosoethoxybenzene.—See A., I, 466.

Polymethylbenzenes. XIX. **Jacobsen reaction.** V. C. L. MOYLE and L. I. SMITH (J. Org. Chem., 1937, 2, 112—137; cf. this vol., 338).—Recorded cases of the Jacobsen rearrangement of alkyl-, halogeno-, and halogenoalkyl-benzenes are collected. Except when halogen alone is present, only tetra- or penta-substituted derivatives rearrange. In the series $\text{C}_6\text{HMe}_4\text{Hal}$ the relative ease of migration is $\text{Br} > \text{Me} > \text{Cl}$, but in the series $\text{C}_6\text{H}_2\text{Me}_3\text{Hal}$ it is $\text{Br} > \text{Cl} > \text{Me}$, and the ease of rearrangement is

much influenced by the conditions and exact nature of the substituent. The effect of varying the nature of the reagent on the rearrangement of $\text{C}_6\text{H}_2\text{Me}_3$ is detailed. Ethyl- ψ -cumene and -mesitylene rearrange, losing the Et. Mechanisms hitherto postulated are shown to be incorrect, as also is that involving formation of CH_2Ph_2 derivatives (since C_6HMe_5 and ψ -cumene give only as much prehnitene as is obtained from C_6HMe_5 alone). *o*- or *p*-Addition of $\text{OH-SO}_3\text{H}$ to give quinonoid compounds capable of rearrangement is possible, but of limited application. Decomp. into free radicals and rearrangement thereof is more probable; this would account also for the tarry material and SO_2 formed during slow rearrangements. With AlCl_3 1:3:4- $\text{C}_6\text{H}_3\text{Me}_2\text{Bu}^i$ gives 45% of 1:3:5- $\text{C}_6\text{H}_3\text{Me}_2\text{Bu}^i$ as sole recognisable product.
R. S. C.

Condensation of aromatic hydrocarbons with methyl chloromethyl ether. Alkylation of aromatic rings. G. VAVON and J. BOLLE (Compt. rend., 1937, 204, 1826—1828; cf. A., 1914, i, 156).—1:3:5- $\text{C}_6\text{H}_3\text{Me}_3$ (I mol.) with $\text{CH}_2\text{Cl-OMe}$ (I) (1.1 mol.) in AcOH at 80° affords a CH_2Cl derivative (II) which is determined by treating the reaction mixture with H_2O [when (I) is rapidly hydrolysed] and titrating free HCl. Many aromatic compounds react, more particularly those containing Me which orients the incoming group *o-p*. Chloromethylation greatly inhibits further reaction. (II) when reduced affords $\text{C}_6\text{H}_2\text{Me}_4$, which by a similar series of reactions is converted into C_6Me_6 .
J. L. D.

Tafel's rearrangement. III. **Structural formula of the hydrocarbon $\text{C}_{12}\text{H}_{18}$ obtained by electrochemical reduction of ethyl benzylmethylacetoacetate.** H. STENZL and F. FIOHTER (Helv. Chim. Acta, 1937, 20, 846—851; cf. A., 1934, 631; 1936; 604).— $\text{CHMeEt-CH}_2\text{-COPh}$ with Zn-Hg and HCl in AcOH affords γ -methyl-n-amylobenzene, b.p. $219^\circ/740$ mm., converted by Br at 150° into $\alpha\beta$ -dibromo- γ -methyl-n-amylobenzene, m.p. 96° , and by way of the sulphonyl chloride into γ -methyl-n-amylobenzene-4-sulphonamide, m.p. 69.5° . CHMePr-CHPh-OH is converted by HI and P into β -methyl-n-amylobenzene (I), b.p. $214^\circ/740$ mm., which similarly affords β -methyl-n-amylobenzene-4-sulphonamide (II), m.p. 86° . $\text{CH}_2\text{Ph-CHEt}_2$ affords β -ethyl-n-butylbenzene-4-sulphonamide, m.p. 89° . (II) is identical with the sulphonamide obtained from the product [which is therefore (I)] of cathodic reduction of $\text{CH}_2\text{Ph-CMeAc-CO}_2\text{Et}$.
P. G. C.

Effect of a high-tension electrical discharge on the catalytic reduction of nitrobenzene.—See A., I, 470.

Applications of fractional distillation to intermediate products in the laboratory. F. R. STAHELIN (Chem. Fabr., 1937, 10, 315—321).—The use of packed and jacketed columns for laboratory-scale working is discussed with reference to the prep. and separation of *o*- and *p*- $\text{C}_6\text{H}_4\text{Cl-NO}_2$ from PhCl , and of *m*- $\text{C}_6\text{H}_4\text{Cl-NO}_2$ from PhNO_2 . The latter reaction in presence of FeCl_3 gave a 72% yield on the PhNO_2 reacting. For nuclear chlorination in presence of Fe catalysts (e.g., the prep. of PhCl from C_6H_6),

Cl_2 should be delivered below the surface of the liquid to avoid additive reaction in the gas phase.

J. S. A.

Reaction of benzyl chloride with mercuric salts.—See A., I, 417.

Hexa-alkylphenylethanes. IV. Bromoalkylbenzenes. J. H. BROWN and C. S. MARVEL (J. Amer. Chem. Soc., 1937, 59, 1176—1178).—Treatment of $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CHO}$ with $\text{MgR}\cdot\text{X}$ yields a carbinol, which when heated with KHSO_4 at $150\text{--}180^\circ$ for 2—5 hr. is partly oxidised to the ketone, but chiefly dehydrated to the olefine. This is reduced (PtO_2 —Pt-black) to p -bromoalkylbenzene, better prepared by direct reduction of the carbinol with I and red P in glacial AcOH . The b.p. are: n -alkyl- p -bromophenylcarbinols, *Bu*- 122— $127^\circ/1$ mm., *heptyl*- 149— $150^\circ/1$ mm., *decyl*- 185— $188^\circ/2$ mm., *dodecyl*- (m.p. 49— 50°); p -bromo- n -alkenylbenzenes, *pentenyl*- 98— $100^\circ/1$ mm., *octenyl*- 145— $155^\circ/1$ mm., *undecenyl*- 166— $169^\circ/1$ mm., *tridecenyl*- 198— $200^\circ/2$ mm. (m.p. 28— 30°); and p -bromo- n -alkylbenzenes, *amyl*- 113— $115^\circ/5$ mm., *octyl*- 125— $126^\circ/1$ mm., *undecyl*- 165— $166^\circ/2$ mm., *tridecyl*- 182— $185^\circ/1$ mm. (m.p. 31— 32°). The p -bromophenyl n -alkyl ketones and their 2:4-dinitrophenylhydrazones respectively melt at: *heptyl*- 68— 69° and 149— 150° , *decyl*- 56— 57° and 113— 114° , *dodecyl*- 63— 64° and 109— 110° (*semicarbazone*, m.p. 107— 108°). Similarly $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{CHO}$ affords m -bromo-phenylmethylcarbinol, b.p. 136— $140^\circ/20$ mm., *-styrene*, b.p. 90— $94^\circ/20$ mm. (dehydration by P_2O_5), and *-ethylbenzene*, b.p. 85— $86^\circ/20$ mm., also prepared from PhEt by nitration, reduction, acylation, bromination, hydrolysis, diazotisation, and replacement of N_2 by H . A. Li.

Peroxide effect in the halogenation of aromatic side chains. M. S. KHARASCH, E. MARGOLIS, P. C. WHITE, and F. R. MAYO (J. Amer. Chem. Soc., 1937, 59, 1405—1406).—The bromination and chlorination of PhMe are greatly accelerated by peroxides. In presence of ascaridole, PhMe (20 mol.) and Br (1 mol.) yield CH_2PhBr (0.83 mol.) in $\frac{1}{2}$ hr. at 25° .

A. Li.

Hexa-alkylphenylethanes. III. Hexa- p -cyclohexylphenylethane and hexa- m -tolylethane. J. H. BROWN and C. S. MARVEL (J. Amer. Chem. Soc., 1937, 59, 1175—1176).— p -Bromocyclohexylbenzene, when treated in Et_2O with Mg followed by Et_2CO_3 , and decomposed by cold saturated NH_4Cl , gives a carbinol which is converted by HCl and CaCl_2 in dry Et_2O into *tri- p -cyclohexylphenylmethyl chloride*, m.p. 146— 147° . This when shaken in PhMe with mol. Ag in absence of air and light affords a deep red solution of *hexa- p -cyclohexylphenylethane* (the colour of which indicates less dissociation than of hexadiphenylethane), rapidly oxidised by air to *tri- p -cyclohexylphenylmethyl peroxide*, m.p. 151— 152° . Similarly *tri- m -tolylmethyl chloride*, m.p. 84— 85° , from $m\text{-C}_6\text{H}_4\text{MeBr}$, yields the orange *hexa- m -tolylethane* (dissociated to about the same extent as the p -compound), oxidised to *tri- m -tolylmethyl peroxide*, m.p. 158— 159° . A. Li.

Structure and electronic interpretation of some optically active sulfoxides. P. SPINOGLIO (Gazzetta, 1937, 67, 264—272).—It is suggested that

the optical activity of mixed sulfoxides (A., 1936, 1031) may be due, not to a semipolar double linking, but to a tetrahedral structure. Optical activity of compounds of $\text{RR}'\text{S}$ with Cl_2 is predicted.

E. W. W.

Salts of sulphinic acids, $\text{R}\cdot\text{SO}_2\text{H}$. J. V. DUBSKÝ and E. ORAVEC (Publ. Fac. Sci. Univ. Masaryk, 1937, No. 232, 10—16).—The following salts were pptd. and analysed: Zn^{++} , Cu^{++} , Ni^{++} ($+2\text{H}_2\text{O}$ replaceable by 2NH_3), Co^{++} ($+2\text{H}_2\text{O}$), and Ag^+ salts of PhSO_2H ; Ag^+ , Hg^{++} , and Fe^{+++} salts of $m\text{-C}_6\text{H}_4(\text{SO}_2\text{H})_2$; Mn^{++} , Cd^{++} ($+3\text{H}_2\text{O}$), Sn^{++} (basic), Zn^{++} ($+3\text{H}_2\text{O}$), Ag^+ , and Fe^{+++} salts of $1\text{-C}_{10}\text{H}_7\cdot\text{SO}_2\text{H}$; Hg^{++} , Cd^{++} , Mn^{++} , Ba^{++} ($+2\text{H}_2\text{O}$), Ag^+ , and Fe^{+++} salts of $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_2\text{H}$. F. R.

Molecular constitution of naphthalene. G. ODDO (Gazzetta, 1937, 67, 216—217; cf. A., 1937, I, 224).—A claim of priority for the suggestion of displacement of C_{10}H_8 linkings during substitution reactions (cf. A., 1925, i, 804).

E. W. W.

Formation of nitrobenzophenones during the nitration of diphenylmethane. J. F. SALELLAS (Anal. Asoc. Quim. Argentina, 1937, 25, 39—43).— CH_2Ph_2 with commercial HNO_3 (d 1.35) gives, in addition to *pp'*- and *op'*- $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, 2—3% of *pp'*- and *op'*- $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$. F. R. G.

Order of introduction of new substituents into the naphthalene nucleus. J. S. JOFFE (J. Gen. Chem. Russ., 1937, 7, 1106—1112).—Substituents are classified as “quinogenic” (OH , NH_2 , etc.) or stabilising (NO_2 , etc.), with halogens occupying an intermediate place. If an α -substituent of the first group is present, further substitution will take place preferentially in the order 2, 4, 5, and 6, whilst when it is at β the order will be 1, 3, 6, and 8. Substituents of the second group stabilise the nucleus into which they are introduced, so that further substitution takes place into the second ring. In addition, order of substitution depends on certain peculiarities of the C_{10}H_8 mol., viz., greater reactivity of the α -H atoms, absence of quinogenic tendency between C_{12} and C_{13} , and the proximity of atoms in the *peri*-position. R. T.

Nitration of tetrahydronaphthalene. J. J. MAKAROV-ZEMLIANSKI and V. P. BIBISCHEV (J. Gen. Chem. Russ., 1937, 7, 1280—1283).—Tetrahydronaphthalene and conc. HNO_3 at $6\text{--}14^\circ$ yield a mixture of 6:8- and 7:8-dinitro-1:2:3:4-tetrahydronaphthalene. R. T.

Action of aqueous bromine on 2-nitrofluorene. L. GUGLIAMELLI and M. R. FRANCO (Anal. Asoc. Quim. Argentina, 1937, 25, 1—38).—Bromination in absence of AcOH (see A., 1933, 401) yields mainly 2-bromo-7-nitro- and 5(or 6)-bromo-2-nitrofluorene (I), m.p. 135— 136° , which in AcOH with $\text{Na}_2\text{Cr}_2\text{O}_7$ gives 5(or 6)-bromo-2-nitrofluorenone, m.p. 190° (*oxime*, m.p. 216° ; *phenylhydrazone*, m.p. $177\text{--}178^\circ$; *semicarbazone*, m.p. 192° ; *p-nitrophenylhydrazone*, m.p. 223°), reduced (in EtOH with NH_3 and H_2S) to 5(or 6)-bromo-2-aminofluorenone, m.p. 199° . (I) in EtOH with SnCl_2 in HCl yields 5(or 6)-bromo-2-aminofluorene (*Ac* derivative, m.p. 174°), which by diazotisation and bromination gives 2:5(or 2:6)-dibromofluorene. The following derivatives of 2-

bromo-7-nitrofluorenone are described: *oxime*, m.p. 247° (decomp.); *semicarbazone*, m.p. >350°; *phenylhydrazone*, m.p. 210—212°; *p-nitrophenylhydrazone*, m.p. 300°; *2-bromo-7-acetamidofluorenone*, m.p. 220°.

F. R. G.

Dissociable oxides of anthracenes. 9-Phenylanthracene and its derivatives. C. DUFRAISSE, L. VELLUZ, and (MME.) L. VELLUZ (Bull. Soc. chim., 1937, [v], 4, 1260—1264).—A more detailed account of work already noted (A., 1936, 1101).

J. L. D.

Dissociable organic oxides. Photo-oxide of mesodiphenylanthracene: formation, dissociation, and properties. C. DUFRAISSE and J. LE BRAS (Bull. Soc. chim., 1937, [v], 4, 349—356; cf. A., 1935, 1233).—*meso*Diphenylanthracene (I) when insolated in C_6H_6 , or better CS_2 , absorbs 95% of the theoretical amount of O_2 (pure gas or from the air) for the formation of its photo-oxide (II), $C_{26}H_{18}O_2$, which when slowly heated to 180° dissociates into its components, 95% of the absorbed O being given up at the pure gas. The process has been repeated 7 times with the same sample of (I), but about 10% of it is decomposed each time. Decomp. of (II) begins at 150°, becoming rapid at 180°. Attempts to convert (I), including treatment with MgI_2 , into a non-dissociable isomeride failed, such changes being considered possible only with the corresponding naphthacene compounds (cf. Enderlin, A., 1936, 1241). Attempts to form a monoxide of (I) failed; (II) with $KI-AcOH$ liberates I corresponding with 2 O.

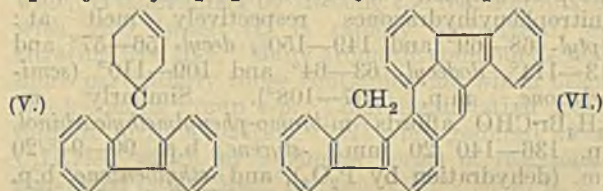
H. G. M.

Synthesis of 1:4-dimethylphenanthrene. R. B. AKIN, G. S. STAMATOFF, and M. T. BOGERT (J. Amer. Chem. Soc., 1937, 59, 1268—1272).—K *p*-xylylacetate (from *p*-xylene) with *o*- $NO_2 \cdot C_6H_4 \cdot CHO$ and Ac_2O yields *o-nitro- α -p-xylylcinnamic acid*, m.p. 173.5—174°, reduced [ammoniacal $Fe(OH)_3$] to the *NH_2-acid*, m.p. 199—200.5°, which when diazotised and treated with Cu powder gives *1:4-dimethylphenanthrene-10-carboxylic acid*, m.p. 199.7—200.2° (*semipicrate*, m.p. 148.5—149°). Heating with Cu in quinoline converts this into *1:4-dimethylphenanthrene* (I), m.p. 50—51° (*picrate*, m.p. 147—148°; *stypnate*, m.p. 135.5—136.5°), which on hydrogenation ($Na + C_6H_{11}OH$) followed by oxidation ($K_2Cr_2O_7$) gives the *quinone*, m.p. 214—216°. (I) is not identical with the compound of Bardhan and Sengupta (A., 1932, 1241), which appears to be the 1:3- Me_2 compound (cf. Bogert and Stamatoff, A., 1933, 948), formed by migration of Me in the fusion with Se, although (I) is unchanged by similar fusion. All m.p. are corr.

A. Li.

Fluorene series. IV. Reactions of diphenylene-ethylene. H. WIELAND and O. PROBST (Annalen, 1937, 530, 274—290).—Polymerisation of diphenylene-ethylene (I) $\begin{matrix} C_6H_5 \\ | \\ C=C \\ | \\ C_6H_5 \end{matrix}$ is accelerated by air, in the presence of which the polymeric hydrocarbon is accompanied by a higher peroxide $(C_{14}H_{10}O_2)_n$, fluorenone, and CH_2O . Polymerisation is the main reaction when a solution of the hydrocarbon is exposed to air in the dark. Autoxidation and polymerisation are restricted by the same substances, notably pyrogallol. (I) with Na in Et_2O

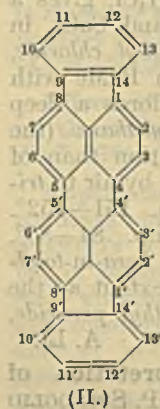
gives an intensely red compound, which is converted by H_2O into $\alpha\delta$ -didiphenylenebutane (II), m.p. 224—225°, and $\alpha\gamma$ -didiphenylenebutane (III), m.p. 171—171.5°. The production of (III) is indirect and due to reduction of (I) to Na 9-methylfluorene (owing to traces of moisture in the Et_2O), which then reacts with (I). The structure of (II) and (III) follows from the reaction of their Na derivatives with CO_2 , whereby respectively $\alpha\alpha'$ -didiphenyleneadipic acid, m.p. 253° (*Me* ester, m.p. 250—251°), decarboxylated to (II) and $\alpha\gamma$ -didiphenylenevaleric acid, m.p. 211—212° (*Me* ester, m.p. 149—150°), decarboxylated to (III), are produced. Treatment of 9-methylfluorene (IV) with Na in Et_2O followed by CO_2 gives 9-methylfluorene-9-carboxylic acid, m.p. 168° (in a non-reproducible experiment a substance, $C_{28}H_{22}O_3$, m.p. 159.5°, was isolated). Hydrogenation (PtO_2 in Et_2O) of (I) affords $\beta\gamma$ -didiphenylenebutane, m.p. 188°, with some (IV); in presence of Pd (IV) is the sole product. 2:7-Dibromo-9-methylfluorene has m.p. 141.5°. Addition of butadiene to (I) gives *diphenylenecyclohexene* (V), m.p. 145.5°, hydrogenated to a substance, m.p. 80—80.5°. (I) and $CHN_2 \cdot CO_2Et$ at 100° give *Et diphenylenecyclopropanecarboxylate*, m.p. 118.5°,



hydrolysed to *diphenylenecyclopropanecarboxylic acid*, m.p. 214—215°; this could not be decarboxylated but *diphenylenecyclopropane*, m.p. 73—73.5°, is readily obtained from (I) and CH_2N_2 . $CPh_2 \cdot CH_2$ and $CHN_2 \cdot CO_2Et$ do not readily yield the pure corresponding ester but 1:1-diphenylenecyclopropanecarboxylic acid, m.p. 171°, is readily purified; when heated with CaO at 300° it yields 1:1-diphenylenecyclopropane, b.p. 140° (bath)/12 mm., more readily obtained from $CPh_2 \cdot CH_2$ and CH_2N_2 . Thermal depolymerisation of (I) is accompanied by the formation of fluorene, (IV), and a hydrocarbon (VI), m.p. 198—199°.

H. W.

Fluoranthene and its derivatives. VI. J. VON BRAUN and G. MANZ (Ber., 1937, 70, [B], 1603—1610).—Treatment of fluoranthene (I) with $NaNH_2$ in boiling decahydronaphthalene yields *periflanthene* (II), m.p. >360°, which could not be obtained by use of $NHPhNa$, by heating with $AlCl_3$ at 200°, with $AlCl_3 + NaCl$, or with S or Se. It is converted by dil. HNO_3 in a sealed tube into non-homogeneous products, but is scarcely attacked by CrO_3 or by air in boiling $C_6H_5Cl_3$. It is unchanged by $Na_2S_2O_4$, metals, and acids or Na and amyl alcohol. Hydrogenation (Ni) of (II) at 270°/250 atm. readily gives the vitreous compound, $C_{32}H_{36}$, b.p. >320°/0.3 mm., which does not give recognisable products when boiled with dil. HNO_3 possibly by reason of simultaneous dehydrogenation to the substance (III), $C_{32}H_{32}$, m.p. 235—238°, also obtained accidentally by hydro-



genation of (II). (III) is dehydrogenated by S (8—9 atoms) to (II) and by Se (2 atoms) at 300° to the compound, $C_{32}H_{28}$, m.p. 314° after softening at 300°. 4-Bromofluoranthene is converted by Cu powder and NaI in N_2 at 300° into difluoranthyl, m.p. 327—329°, which gives (II) when heated with $NaNH_2$, thus supporting the constitution assigned to the latter. 4-Ketotetrahydrofluoranthene and $MgMeI$ give a product converted by boiling 20% H_2SO_4 into 4-methyldihydrofluoranthene, b.p. 160—170°/0.2 mm., m.p. 127—128°, whence 4-methylfluoranthene (IV), m.p. 66° (picrate, m.p. 172°). 4-Phenyldihydrofluoranthene, b.p. 220—230°/0.3 mm., m.p. 148°, is dehydrogenated by Cu turnings in H_2 at about 600° to 4-phenylfluoranthene (V), m.p. 144°. Neither (IV) nor (V) resembles (I) in behaviour towards $NaNH_2$, thus leading further support to the constitution assigned to (II). Acenaphthene and acenaphthylene are not influenced by $NaNH_2$; tetrahydronaphthalene is largely resinified whilst stilbene is mainly converted into $CH_2Ph \cdot CH_2Ph$ with production of phenanthrene. (II) appears to be converted by fuming HNO_3 at -2° into an amorphous NO_2 -derivative and to be sulphonated by conc. H_2SO_4 at 100°. It does not react with maleic anhydride. It gives a dark violet powder when heated with $AlCl_3 + NaCl$. H. W.

Synthesis of 1:2-benzanthracene derivatives related to 3:4-benzpyrene. M. S. NEWMAN (J. Amer. Chem. Soc., 1937, 59, 1003—1006).—5:9-Dimethyl- (I) and 9-methyl-1:2-benzanthracene (II) are synthesised. (I) is probably as carcinogenic as the 10-Me compound, but (II) appears to be less potent. In contrast to the course of the Friedel-Crafts reaction, 1- $C_{10}H_7 \cdot MgBr$ and 3:1:2- $C_6H_3Me(CO)_2O$ (prep. from perylene and maleic anhydride by way of the H_2 -anhydride, m.p. 61—62°, b.p. 155—156°/12 mm., dehydrogenated by S at 250—260°), m.p. 115—116°, afford 52% of 3- α -naphthoyl-o-, m.p. 165.6—166.8°, and only 1.5% of 2- α -naphthoyl-m-toluic acid, m.p. 234—235° (sinters at 230°), the structures of which are proved by decarboxylation. The o-toluic derivative with $MgMeBr$ gives 74% of the lactone, m.p. 131.6—132°, of 3- α -hydroxy- α -1'-naphthylethyl-o-toluic acid, reduced by Zn-Hg in HCl -AcOH to 3- α -1'-naphthylethyl-o-toluic acid, m.p. 162—162.6°, which by ring-closure with H_2SO_4 at 20°, followed by reduction by Zn-NaOH, gives a poor yield of (I), m.p. 135—135.5°. o- α - $C_{10}H_7 \cdot CO \cdot C_6H_4 \cdot CO_2H$ affords similarly the lactone, m.p. 154.5—155°, of o- α -hydroxy- α -1'-naphthylethylbenzoic acid, o- α -1'-naphthylethylbenzoic acid, m.p. 169.4—170°, and a 26% yield of (II), m.p. 138.4—138.8°. o- $C_6H_4Me \cdot CO \cdot C_{10}H_7 \cdot \alpha$ exists in forms, m.p. 59—61° and (unstable) 51.5—52.5°. M.p. are corr.

R. S. C.

Condensation of acetylene with aromatic amines in presence of mercury salts. XII. N. KOZLOV and D. MITZKEVITSCH (J. Gen. Chem. Russ., 1937, 7, 1082—1085).—The reaction is represented: $NH_2Ph + C_2H_2 + HgCl_2 \rightarrow xNH_2Ph \cdot yHgCl_2 \cdot zC_2H_2 \rightarrow 2NPh \cdot CHMe \rightarrow NHPh \cdot CHMe \cdot CH_2 \cdot CH \cdot NPh \rightarrow NHPh \cdot CHMe \cdot CH_2 \cdot CH \cdot NPh$. The reaction is catalysed equally well by $HgCl_2$, $HgCl_2 \cdot 2NH_2Ph$, $C_2H_2 \cdot 3HgCl_2 \cdot 3HgO$, or $C_2H_2 \cdot HgCl_2$. R. T.

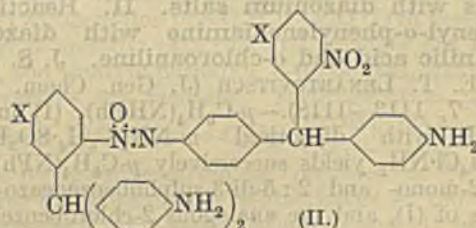
Action of benzoyl chloride on sodium azide in contact with alkali. G. LABRUTO and A. LANDI (Gazzetta, 1937, 67, 213—216).— NaN_3 , $BzCl$, and solid KOH give $CO(NHPh)_2$ (I), with traces of $PhNCO$, presumably by the reactions $NaN_3 \rightarrow BzN_3 \rightarrow PhNCO + N_2$; $PhNCO + KOH \rightarrow NH_2Ph + K_2CO_3$; $PhNCO + NH_2Ph \rightarrow$ (I). E. W. W.

Products of bromination of d-tartaric acid di-p-toluidide. H. KUCZYŃSKI (Rocz. Chem., 1937, 17, 186—188; cf. this vol., 176).—The substance described by Wróbel (*ibid.*, 77) as 2:2'-dibromo-3:3'-diketo-5:5'-dimethyldihydro-2:2'-di-indolyl, m.p. 74°, is actually 2:6-dibromo-p-toluidine, and that described as 2-(2'-bromo-3'-keto-5'-methyl-2:2'-indolyl)-3-keto-5-methylindolenine, m.p. 210°, is probably tartaric acid di-2-bromo-p-toluidide.

R. T.

Complex salts with trans-1:2-diaminocyclohexane.—See A., I, 474.

Condensation of o-nitrobenzaldehydes with aniline. III. Photochemical behaviour of the anthranils and triphenylmethanes obtained. I. TANASESCU and (MLLE.) M. SUCIU (Bull. Soc. chim., 1937, [v], 4, 245—258; cf. A., 1936, 1509).—A mechanism involving tautomerism of the nitro-aldehyde is proposed for the condensation of o-nitrobenzaldehydes with NH_2Ph sulphate in presence of $ZnCl_2$ to give a triphenylmethane and a p-aminophenylantranil (cf. A., 1906, i, 515). 5-Chloro-2-nitro-4':4''-diaminotriphenylmethane (I) when irradiated in C_6H_6 with sunlight gives a blue compound and a compound, $C_{38}H_{30}O_2N_6Cl_2$, m.p. 78—80° (Ac derivative; Bz_3 derivative, m.p. 157°), probably (II) ($X = Cl$), reduced by $Sn-HCl$ to



2:4':4''-triaminotriphenylmethane. Similarly, 2-nitro-4':4''-diaminotriphenylmethane (III) gives a blue compound and a compound, $C_{38}H_{32}O_2N_6$, m.p. 125°, considered to be (II) ($X = H$). The substances (II) ($X = H$ and Cl) when irradiated in C_6H_6 with sunlight give the corresponding blue compounds, and like (I) and (III) slowly give a blue ppt. with H_2O_2 - HCl in the cold and a brown ppt. when the solution is heated. o-Nitrobenzylidene chloride (IV) when treated with $AlCl_3$ - CS_2 and $PhCl$ gives 2-nitro-4':4''-dichlorotriphenylmethane (V), m.p. 110°, also obtained (Sandmeyer) from (III), and converted by $NH_3 \cdot H_2O$ - $EtOH$ - $CuSO_4$ (sealed vessel; 15 hr.; 180°) into a compound, $C_{27}H_{23}ON_3$, m.p. 240—250°, probably 2-diethylamino-5-p-diethylaminophenylacridine N-oxide. Attempts to prepare 2-nitrotriphenylmethane-4':4''-dicarboxylic acid from (V), KCN , $Cu_2(CN)_2 \cdot H_2O$ - $EtOH$ (sealed tube; 190—200°; 15 hr.), and from (IV), $AlCl_3$ - CS_2 , and $PhCN$, failed; the latter gave a compound, $C_{14}H_{11}O_4N_2Cl$, m.p. 180° (sublimes in vac. giving a substance, m.p. 225.5°), considered to be

m-NO₂·C₆H₄·CHCl·C₆H₄·CO·NH·OH-*p*. 2-Chloro-*p*-aminophenylantranil (VI) is converted by the diazo-reaction into 2 : 4'-dichlorophenylantranil, m.p. 202°, which with H₂SO₄·NaNO₂ at -10° gives 2 : 7-dichloroacridone, m.p. 416°. This when treated with NPhMe₂·POCl₃ (water-bath) gives 2 : 7-dichloro-5-*p*-dimethylaminophenylacridine, m.p. 240°. Attempts to prepare (VI) from *o*-NO₂·C₆H₄·CHO, NH₂Ph, and AcOH·POCl₃ failed, complex products being obtained.

H. G. M.

Some nitro- and amino-derivatives of benz-anilide, thiobenzanilide, and 1-phenylbenzthiazole, and the azo colours derived from them. H. RIVIER and J. ZELTNER (Helv. Chim. Acta, 1937, 20, 691—704).—Azo-compounds are prepared on cotton from β-C₁₀H₇·OH as coupling component, and NH₂-derivatives of NPhBz, NPh·CSPH, and 1-phenylbenzthiazole (I) as azo-components. It is concluded that the CO group increases the depth of colour slightly, the CS group greatly, but S is easily removed by acids; the effect of the thiazole group is intermediate. The dyes from H-acid and derivatives of NPhBz and (I) as azo-components dye wool in red to blue-violet shades, but no correlation similar to that found with the dyes from β-C₁₀H₇·OH can be drawn. Dyes could not be prepared from H-acid and derivatives of NPhBz·CSPH owing to loss of S under the acid conditions necessary for coupling. The following are described: *m*-, m.p. 134—134.5°, and *p*-nitro-, m.p. 154.5—155°, and *m*-amino-thiobenzanilide, m.p. 130—131°; thiobenz-*m*-nitroanilide, m.p. 150°; 3', m.p. 139°, 4', m.p. 156°, 4-, m.p. 206°, and 5-amino-1-phenylbenzthiazole, m.p. 205°.

P. G. C.

Reaction of *p*-phenylenediamine and its derivatives with diazonium salts. II. Reaction of diphenyl-*o*-phenylenediamine with diazotised metanilic acid and *o*-chloroaniline. J. S. JOFFE and E. T. LENARTOVITSCH (J. Gen. Chem. Russ., 1937, 7, 1113—1118).—*p*-C₆H₄(NPh)₂ (I) in 80% AcOH with diazotised *m*-NH₂·C₆H₄·SO₃H or *o*-C₆H₄Cl·NH₂ yields successively *p*-C₆H₄(NPh)₂ and the 2-mono- and 2 : 5-di-3-sulphobenzenazo-derivatives of (I), and the analogous 2-chlorobenzenazo-derivative.

R. T.

Configurations of the isomeric diazocyanides. R. J. W. LE FEVRE and H. VINE (Chem. and Ind., 1937, 688).—Determination of the dipole moments of the two *p*-bromobenzene diazocyanides, m.p. 42° and 130°, respectively, indicates that the form of lower m.p. is the *trans*- and that of higher m.p. is the *cis*-variety. The conversion *trans* → *cis* proceeds spontaneously in C₆H₆ at room temp. It is probable that the structures assigned by Hantzsch to the diazocyanides should be interchanged and that these compounds are examples of geometrical isomerism, like that of C₂H₂Cl₂, in which the *trans*- is the less stable of the two isomerides.

H. W.

Diazo-chemistry. H. A. J. SCHOUTISSEN (Chem. Weekblad, 1937, 34, 506—515).—A review. S. C.

Diaryls and their derivatives. XIV. Ring-closure in 6 : 6'-dinitro-2 : 2'-dihydroxy-1 : 1'-dinaphthyl. J. S. JOFFE and I. S. GORELIK (J. Gen. Chem. Russ., 1937, 7, 1102—1105).—Attempted

synthesis of 5 : 8-dinitro-1 : 12-dihydroxyperylene by heating 6 : 6'-dinitro-2 : 2'-dihydroxy-1 : 1'-dinaphthyl (I) or its Pb salt with AlCl₃ at 120—180° for 0.5—12 hr. was unsuccessful. (I) with H₂SO₄ at 40° (30 min.) gives 6 : 6'-dinitro-1 : 1'-dinaphthylene 2 : 2'-oxide.

R. T.

Hydrogenation of αβ-dihydroxypropiophenone. Formation of two diastereoisomeric phenylglycerols. M. CAHNMANN (Bull. Soc. chim., 1937, [v], 4, 226—232; cf. A., 1936, 68).—CH₂:CH·COPh when treated with H₂O₂·MeOH·NaOH at 0—10° gives *epoxypropiophenone*, m.p. 53° (at higher temp. COPhMe is chiefly formed), which when refluxed (3—4 hr.) with 0.01*N*-HCl gives αβ-dihydroxypropiophenone, m.p. 81.5° (corr.). This when reduced by Al-Hg-H₂O or hydrogenated (Pd-C-H₂) gives a mixture of two diastereoisomerides, since on benzylation it yields both α- and β-tribenzoates of α-phenylglycerol (cf. A., 1934, 649).

H. G. M.

Sex hormones : their relationships with cholesterol. R. DELABY (J. Pharm. Chim., 1937, [viii], 26, 136—165).—A lecture.

Cholesterol and the adrenal cortical hormone.—See A., III, 360.

Process of irradiation of compounds of the ergosterol type. K. DIMROTH (Ber., 1937, 70, [B], 1631—1636).—The comparative behaviour of ergosterol (I) and lumisterol (II) when subjected to very short irradiation shows that (II) is an essential intermediate in the conversion of (I) into trachysterol. Irradiation of 22-dihydroergosterol, 7-dehydrocholesterol, and 7-dehydrositosterol gives products with antirachitic activity. The changes in the spectra proceed analogously and it is therefore very probable that intermediate stages are passed through as with (I). All these sterols have two conjugated double linkings between C₅ and C₆, and between C₇ and C₈; this conjugated system is essential for the incidence of the photo-reaction. The course of irradiation of pyrocalciferol (III) and isopyrocalciferol (IV) differs completely from that of (I) or (II) since there is no evidence of the formation of intermediate products with characteristic absorption between 248 and 320 mμ. The final products cannot contain conjugated double linkings. (III) gives *photopyrocalciferol* (V), m.p. 103—105° (indef.), [α]_D²⁰ +50.8° in CHCl₃ (*dinitrobenzoate*, m.p. 162°, [α]_D²⁰ +51.7° in CHCl₃; *isobutyrate*, m.p. 79—80°; non-cryst. *acetate*), which does not give a ppt. with digitonin (VI) in 90% EtOH and absorbs 2 H₂ when hydrogenated. (IV), as *acetate*, affords *photoisopyrocalciferol* (VII), m.p. (indef.), 76—80°, [α]_D²⁰ -60.4° in CHCl₃, which does not give a ppt. with (VI) (*dinitrobenzoate*, m.p. 145—146°, [α]_D²⁰ -11.2° in CHCl₃; *acetate*, m.p. 70°, [α]_D²⁰ -56.3° in CHCl₃). When heated at 188° (V) is transformed into (III) and (VII) into (IV) so that it appears that only one double linking has wandered during irradiation. Under similar conditions supra-sterol II and the irradiation product from dehydroergosterol are unchanged. Oxidation of (IV) or *photoisopyrocalciferol* *acetate* with conc. HNO₃ does not yield C₆HMe(CO₂H)₄.

H. W.

Sex hormones. XXIII. Action of selenium dioxide on Δ^5 -androstenediol. L. RUZICKA and P. A. PLATTNER (Helv. Chim. Acta, 1937, 20, 809—811).— Δ^5 -Androstene-3-*trans*-17-*trans*-diol with SeO_2 in H_2O -AcOH affords Δ^5 -androstene-3:4:17-*triol*, m.p. 253—254° (*triacetate*, m.p. 156—156.5°). Catalytic reduction affords *androstane*-3:4:17-*triol*, m.p. 260—261° (*triacetate*, m.p. 222.5—223.5°).

P. G. C.

Synthetic experiments in the pinane group. III. Synthesis and configuration of pinic acid. P. C. GUHA, K. GANAPATHI, and U. K. SUBRAMANIAN (Ber., 1937, 70, [B], 1505—1512).—Pinonic acid obtained from Greek oil of turpentine appears to be a mixture of *cis*- and *trans*-forms. From Et pinonate, two semicarbazones, m.p. 154—155°, and m.p. 129—134°, are obtained; the former of these gives homogeneous Et pinonate, b.p. 127°/2—3 mm., the pinonic acid from which is oxidised to *trans*-pinic acid (I), b.p. 203°/4 mm. [*Et*₂ ester (II), b.p. 146°/10 mm.; *dianilide* (III), m.p. 204°; *diamide*, m.p. 222—223°]. The *trans*-nature of (I) follows from its production by the oxidation of *trans*-1-hydroxymethyl-3- β -hydroxyethyl-2:2-dimethylcyclobutane, b.p. 145—146°/8 mm., obtained by reduction of (II) with Na and abs. EtOH. Reduction of *cis*-norpinic anhydride could not be effected by Na-Hg or by Zn with HCl or AcOH whereas Na and abs. EtOH gives *Et* 2:2-dimethyl-3-hydroxymethylcyclobutane-1-carboxylate (IV), the *trans* nature of which is established by its oxidation by KMnO_4 to *trans*-norpinic acid. The acid from (IV) is converted by the successive action of PBr_3 and $\text{C}_6\text{H}_5\text{-EtOH}$ into *Et* 2:2-dimethyl-3-bromomethylcyclobutane-1-carboxylate, b.p. 110°/5 mm., converted by NaCN in EtOH into *Et* 2:2-dimethyl-3-cyanomethylcyclobutane-1-carboxylate, b.p. 125—126°/7 mm., hydrolysed by $\text{KOH-H}_2\text{O}$ to (I). *cis*-Norpinic acid is converted by the successive action of SOCl_2 and $\text{NH}_3\text{-C}_6\text{H}_6$ into *cis*-norpindiamide, m.p. 188—189°.

H. W.

Polar and non-polar form of *o*-, *m*-, and *p*-aminobenzoic acids. P. SPINOGLIO (Gazzetta, 1937, 67, 256—264).—The compounds (presumably thiocarbamides) from *o*- (I), *m*- (II), and *p*- $\text{NH}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$ (III) with $\text{CH}_2\text{-CH}_2\text{-NCS}$ are prepared. That from (I) is obtained in EtOH at room temp., at which (I) is presumed to be in the non-ionised neutral form; (II) and (III) react when heated. The solubility of the three acids in H_2O increases to a max. with the addition of inorg. salts. The greatest increase is observed with (II), in which it is suggested that there is the greatest proportion of the double ion $\text{NH}_3^+\text{-C}_6\text{H}_4\text{-CO}_2^-$, to which the solubility effect is ascribed.

E. W. W.

Friedel-Crafts reaction of lactones. II. Aromatic substituted fatty acids from δ -chloro- γ -valerolactone. H. BEYER (Ber., 1937, 70, [B], 1482—1491).—The action of AlCl_3 on δ -chloro- γ -valerolactone and PhMe at 70—80° gives unchanged material, δ -*p*-tolyl-*n*-valeric acid, b.p. 146—148°/0.1 mm., m.p. 74° after softening at 71—73° (*amide*, m.p. 113—114°), γ -*di*-*p*-tolyl-*n*-valeric acid (I), b.p. 195—197°/0.1 mm., a mixture of 2:6- and 2:7-

dimethylantracene [identified by ozonisation to 2:7-dimethylantracene-10-butyric acid (II)], and 2:7-dimethylantracene-10-butyric acid (III), m.p. 187—189° after softening at 185° (apparently accompanied by the isomeric 2:6-compound). (I) affords a *Me*, b.p. 169—171°/0.2 mm., and *Et*, b.p. 178—179°/0.1 mm., ester and is converted by PCl_5 followed by AlCl_3 in CS_2 into 1-*keto*-4-*p*-xylyl-7-methyl-1:2:3:4-tetrahydronaphthalene, b.p. 175—176°/0.1 mm. [*semi*-carbazone, m.p. 208—210° (decomp.) after softening at 205° or m.p. 212—214° (decomp.) when rapidly heated]. (III) affords a *Me*, m.p. 116—118°, and an *Et*, m.p. 83—85° (decomp.), ester which could not be hydrogenated (PtO_2 in EtOH) and a *hydrazide*, m.p. 207—208°. It is reduced ($\text{H}_2\text{-PtO}_2\text{-AcOH}$) to 2:7-dimethyl-1:2:3:4-tetrahydroanthracene-10-butyric acid, m.p. 143—154° after softening at 140°, which, unlike (III), does not fluoresce in solution. Ozonisation of (III) in CHCl_3 yields (II). Treatment of (III) with maleic anhydride at 120—150° gives the adduct, $\text{C}_{24}\text{H}_{22}\text{O}_5$, m.p. 221—223° (decomp.) after softening at 218°.

H. W.

Isolation of *p*-coumaric acid from green tea. M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 32, 138—142).—Hot aq. COMe_2 extracts *p*-coumaric (*p*-hydroxycinnamic) acid [*Ac* derivative, m.p. 208°, *Me* ether, m.p. 171° (*Me* ester, m.p. 89°)]. These derivatives are identical with those prepared synthetically.

J. L. D.

Velocity of catalytic hydrogenations.—See A., I, 470.

Phthalide. I. Hydrogenation of phthalic anhydride. P. R. AUSTIN, E. W. BOUSQUET, and W. A. LAZIER (J. Amer. Chem. Soc., 1937, 59, 864—866).—Hydrogenation of *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ (I) in presence of different metallic catalysts and solvents has been studied, and yields of phthalide, *o*-toluic acid, and their H_6 -derivatives are recorded. Hydrogenation probably occurs by way of *o*- $\text{C}_6\text{H}_4\text{-C}(\text{OH})(\text{OEt})\text{=O}$ in EtOH. By hydrogenation in presence of Ni on kieselguhr 5-nitrophthalide in abs. EtOH at 150°/100 atm. gives 85% of 5-aminophthalide and (I) in aq. NaOH at 110°/100 atm. gives 80% of phthalide.

R. S. C.

spiro-Compounds. III. Synthesis of cyclohexanespirocyclobutane derivatives by the application of the Dieckmann reaction to esters of the tricarballylic series. N. N. CHATTERJEE (J. Indian Chem. Soc., 1937, 14, 127—132).—The cyanohydrins of COMe_2 , cyclopentanone, cyclohexanone, 2-, 3-, and 4-methylcyclohexanone were condensed with Et sodiocyanoacetate and the Na salts of the Et cyanoacetates obtained treated with $\text{CH}_2\text{Br-CO}_2\text{Et}$ to give cyanosuccinates, which on hydrolysis yield the corresponding carballylic acid derivatives. Only those carballylic acids derived from cyclohexanones could be cyclised by means of Na in xylene to cyclobutane derivatives. The following are described: *Et*₂ 1-cyanocyclohexane-1-cyanosuccinate, b.p. 200—205°/7 mm.; 1-carboxycyclohexane-1-succinic acid, m.p. 187° (decomp.) (*Et*₂ ester, b.p. 174—176°/6 mm.); *Et*₂ cyclohexanespirocyclobutane-2-one-3:4-dicarboxylate, b.p. 178—180°/6 mm.; *Et*₂ 4-methyl-

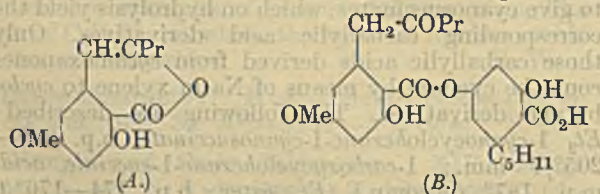
cyclohexane-1-cyano-1-succinate, m.p. 90°; 4-methylcyclohexane-1-carboxylic-1-succinic acid, m.p. 188°; Me_3 4-methylcyclohexane-1-carboxylate-1-succinate, b.p. 178—180°/5 mm.; 4'-methylcyclohexanespirocyclobutan-2-one-3:4-dicarboxylate, b.p. 177—185°/5 mm.; Et_2 1-cyano-2-methylcyclohexane-1-cyano-succinate, b.p. 200—208°; 2-methylcyclohexane-1-carboxylic-1-succinic acid (Et_3 ester, b.p. 175—176°); Et_2 1-cyano-3-methylcyclohexane-1-cyanosuccinate, b.p. 200—205°/6 mm.; 3-methylcyclohexane-1-carboxylic-1-succinic acid (Et_3 ester, b.p. 178°/5 mm.); Et_2 1-cyanocyclopentane-1-cyanosuccinate, b.p. 197—203°/7 mm.; cyclopentane-1-carboxylic-1-succinic acid, m.p. 159° (Et_3 ester, b.p. 173—175°/7 mm.); Et_2 β -dicyano- β -methylbutane- $\gamma\delta$ -dicarboxylate, b.p. 180—182°/6 mm.; $\alpha\alpha$ -dimethyltricarballic acid, m.p. 156° (Et_3 ester, b.p. 160°/5 mm.). D. J. B.

Attempted synthesis of $\alpha\beta$ -dicinnamoylthane. W. LAMPE, E. BLENDERÓWNA, and A. BLUMAN (Rocz. Chem., 1937, 17, 216—225).—

$CHPh:CH:CO:CH_2:CH_2:CO_2Et$ and Ac_2O at 140° yield 5-keto-2-styryl-4:5-dihydrofuran (I), which with $PhCHO$ in $EtOH$ at 100° gives 5-keto-4-benzylidene-2-styryl-4:5-dihydrofuran, m.p. 164—165°. Attempted condensation of (I) with cinnamoyl chloride (II) was unsuccessful. Me sodioacetacetate and (II) in Et_2O yield Me α -cinnamoylacetacetate (III), m.p. 49—50°, and Me α -cinnamoyl- β -O-cinnamoylacetacetate, m.p. 117—119°. (III) and aq. NH_3 at 50° afford Me cinnamoylacetate, m.p. 71—73°, which when treated successively with Na and I gives Me_2 $\alpha\beta$ -dicinnamoyl-succinate (IV), m.p. 135—137°, hydrolysis of which (20% K_2CO_3 at 100°, 1% $EtOH-KOH$ at the b.p., or autoclaving at 3 atm.) yields 4-keto-3-carbomethoxy-4-cinnamoyl-2-styryl-4:5-dihydrofuran, m.p. 240—245°, instead of the expected $\alpha\beta$ -dicinnamoylsuccinic acid. (IV) in $AcOH$ and H_2SO_4 at 100° yield 3:4-dicarbomethoxy-2:5-distyrylfuran, $+H_2O$, m.p. 293°. Sodiocinnamoylacetone and I in Et_2O yield $\alpha\beta$ -dicinnamoyl- $\alpha\beta$ -diacetylthane, m.p. 200°, converted by heating with aq. $AcOH$ and H_2SO_4 into 3:4-dicinnamoyl-2:5-dimethylfuran, m.p. 135—136° [di-oxime, m.p. 262—263° (decomp.)]. The synthesis of $\alpha\beta$ -dicinnamoylthane by any of the above approaches was unsuccessful. R. T.

Reactions of rare earths and allied elements with pyrogallol, gallic acid, and morphine.—See A., I, 477.

Lichen substances. LXXXI. Glomelliferic acid. I. Y. ASAHINA and H. NOGAMI (Ber., 1937, 70, [B], 1498—1499).—Extraction of the thalli of *Parmelia glomellifera*, Nyl, with Et_2O yields glomelliferic acid (I), m.p. 143—144°, which is $C_{25}H_{20}O_8$ since it is converted by cold 10% KOH into glomellin



(II), m.p. 85°, and olivetolcarboxylic acid. The inability of (I) to give a red colour with $CaOCl_2$, the

absence of CO_2H from (II), and the similarity of (I) with microphyllic acid in behaviour towards alkali leads to the constitutions A and B for (II) and (I), respectively. H. W.

Lichen substances. LXXX. Components of so-called *Thamnolia vermicularis*, f. *taurica*. Y. ASAHINA and M. YASUE (Ber., 1937, 70, [B], 1496—1497).—Thalli of *Thamnolia subvermicularis*, Y. Asahina, are extracted with Et_2O and $COMe_2$, and the extracts treated with NH_2Ph in $COMe_2$ and evaporated. The product after washing with dil. $AcOH$ is extracted with Et_2O , whereby squamatic acid (I), m.p. 228° (decomp.), remains undissolved. The mother-liquors contain the anil, m.p. 211°, of baecomycic acid from which the free acid, m.p. 223°, is obtained by treatment with 10% HCl . (I) (Me_2 ester, m.p. 183°) is isolated from *Cladonia squamosa*, f. *denticollis* from Europe. H. W.

Cannizzaro reaction. K. F. BONHOEFFER and H. FREDENHAGEN (Naturwiss., 1937, 25, 459).—When the Cannizzaro reaction is carried out with $PhCHO$ in alkaline solution containing D_2O , the CH_2 of the $CH_2Ph:OH$ formed contains no D. This result indicates that the H is transported directly from the C of one CHO to the other and that the transport of H does not take place after hydration of one of the aldehyde mols. nor does the solvent play a part in its transference. W. O. K.

β -Carotenal, a degradation product of β -carotene. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1937, 20, 682—690).—The mixture obtained by oxidation of β -carotene with $KMnO_4$ contains chiefly β -carotenal (I), deep violet crystals, $C_{30}H_{40}O$, m.p. 139° [oxime, m.p. 180°; semicarbazone, m.p. 212° (sinters 205°)], to which is assigned the formula



a substance (II), m.p. 170°, and other products. In physical properties (I) resembles citraurin (III) (A., 1936, 1435), which, it is suggested, is the 3-OH-derivative of (I). The absorption max. of (I), (II), and (III) in various solvents are given. (I) shows vitamin-A activity. P. G. C.

Velocity of reaction of aldehydes with ketones. V. Reaction of vanillin with acetone. E. K. NIKITIN and S. A. VERSCHINSKI (J. Gen. Chem. Russ., 1937, 7, 1306—1314).—Vanillin in $EtOH$ and aq. $COMe_2$ with 16% aq. KOH yield vanillylideneacetone; the velocity of the reaction \propto concns. of vanillin and $COMe_2$. A method for determination of the substrates, based on the above reaction, is described. R. T.

Indones. XV. Chloro-derivatives of 3-phenyl-2-ethylindone. R. DE FAZI and F. PIRRONE (Gazzetta, 1937, 67, 207—213; cf. this vol., 294).—3-Phenyl-2-ethylindone (crystal data recorded), with Cl_2 in $CHCl_3$ at -15° , gives 2:3-dichloro-3-phenyl-2-ethylhydrindone (I), m.p. 94—96°, with an isomeride (II), m.p. 115—116°, both of which have one labile Cl ; also a substance $C_{17}H_{14}OCl$ (sic), m.p. 119—120°, and two isomerides of the last, m.p. 127—128° and 132—133°. Crystal data of the last two are recorded.

In CCl_4 at -5° , (I), (II), and two substances, $\text{C}_{17}\text{H}_{14}\text{OCl}$ (*sic*), m.p. $105-106^\circ$ and $145-146^\circ$, are obtained.

E. W. W.

Tautomerism of derivatives of acetomesitylene. E. P. KOHLER and R. B. THOMPSON (J. Amer. Chem. Soc., 1937, 59, 887-893).—The persistence of the enolic form of 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ (I) is proved by alkylation of the Mg derivative and other reactions; the amount of *O*-alkyl derivative formed from such systems is a measure of the persistence of the enol form. Reduction of $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ catalytically and by Zn-acid is proved to be a 1:4-addition, which is thus considered to be general both for reduction and for addition of MgRX to the system, $\text{C}\cdot\text{C}\cdot\text{CO}$. Addition first of $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$ to MgPhBr in Et_2O and then of $\text{CH}_2\text{Cl}\cdot\text{OME}$ gives 30% of α -methoxymethoxy- $\gamma\gamma$ -diphenylpropenylbenzene, m.p. $64-65^\circ$ (formed from the enolic form), and 70% of β -methoxy- $\beta'\beta'$ -diphenylisobutyrophenone (II), m.p. $131-132^\circ$, with a little Ph_2 and $\text{CH}_2\text{Ph}\cdot\text{OME}$. (II) is stable to dil. acids and alkali, but with hot 50% HBr gives β -bromo- $\gamma\gamma$ -diphenylisobutyrophenone, m.p. 163° , converted by $\text{KOH}\cdot\text{EtOH}$ into *Ph* α -benzhydrylvinyl ketone, m.p. 115° (dibromide, m.p. 105° , debrominated by $\text{KI}\cdot\text{MeOH}$), which does not polymerise or autoxidise, but is oxidised by KMnO_4 and is reduced by $\text{H}_2\cdot\text{PtO}_2$ to $\text{CHPh}_2\cdot\text{CHMe}\cdot\text{COPh}$. With conc. NaOEt the Br-ketone gives a little *Ph* $\beta\beta$ -diphenyl- α -methylvinyl ketone, m.p. 114° , stable to KMnO_4 . The Mg derivative of (I), however, prepared *in situ*, with $\text{CH}_2\text{Cl}\cdot\text{OME}$ gives 77-80% of α -methoxymethoxy- $\gamma\gamma$ -diphenylpropenylmesitylene (from the enolic form), m.p. 92° , and only 18-20% of β -methoxy- $\beta'\beta'$ -diphenyl-2:4:6-trimethylisobutyrophenone, m.p. 155° ; the last-mentioned ketone, in contrast to (II), is converted by 50% HBr or $\text{KOH}\cdot\text{MeOH}$ directly into mesityl α -benzhydrylvinyl ketone, m.p. $109-110^\circ$ (reduces KMnO_4 ; decolorises Br). Decomp. of the Mg derivative of (II) gives solutions, shown by Br-titration to contain 90-95% of enol; crystallisation gives only the keto-form, but the presence of the enol is confirmed by ready absorption of O_2 to form the peroxide, $\text{CHPh}_2\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{C}_6\text{H}_2\text{Me}_3$, m.p. $116-117^\circ$,

the cyclic nature of which is shown by absence of acidic properties; the peroxide decomposes when heated into $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$ and $\text{CHPh}_2\cdot\text{CHO}$, and is reduced by $\text{H}_2\cdot\text{PtO}_2$ or $\text{KI}\cdot\text{AcOH}$ to α -hydroxy- $\beta\beta$ -diphenylpropionylmesitylene (III), m.p. 76° (acetate, m.p. 89° ; benzoate, m.p. $114-115^\circ$). The dienol (IV) from this OH-ketone, which is obtained from the Mg_2 derivative (2 mols. of CH_4 liberated), is an energetic reducing agent; it is persistent in solution, but could not be isolated as it autoxidises readily. Its existence is proved by reaction of its parent Mg_2 derivative with AcCl and BzCl to give $\alpha\beta$ -di-acet-, forms, m.p. $127-128^\circ$ and 149° , and -benzoyl-oxy- $\gamma\gamma$ -diphenylpropenylmesitylene, m.p. 157° ; by promoting ketonisation by addition of a base or, better, by stopping oxidation by addition of a reducing agent ($\text{Zn}\cdot\text{AcOH}$) it is converted into α -hydroxy- β -keto- $\gamma\gamma$ -diphenylpropylmesitylene (V), m.p. $77-78^\circ$, the isomeride of (III). (III) or (V) with CrO_3 gives mesityl benzhydryl diketone, m.p. $74-75^\circ$, also obtained with 3-4% of a hydrocarbon, (?) an indene derivative, m.p.

212° , by aerial oxidation of the dienol. The solid diketone is stable; it enolises very slowly, since its alcoholic solution barely absorbs O_2 except in the presence of alkali, which rapidly causes equilibration of the keto- and enol (VI), m.p. 117° (phenylurethane, m.p. 148°), forms. It is reduced by $\text{H}_2\cdot\text{PtO}_2$ in MeOH or MgEtBr to the dienol (IV) and treatment with the latter reagent, followed by AcCl , affording the diacetate of the dienol; dissolution in 2% $\text{KOH}\cdot\text{MeOH}$, followed by addition to an excess of 2*N*-HCl, gives a quant. yield of the enolic form (VI). The enol (VI) is only slowly oxidised when solid, but in solution absorbs O_2 more rapidly to yield COPh_2 , $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$, and $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CO}_2\text{H}$; it gives an *O*-acetate, m.p. $86-87^\circ$, and *O*-benzoate, m.p. 124° , reduced by $\text{Zn}\cdot\text{AcOH}$ to the esters of $\text{CHPh}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$. The diketone and its enol (VI) are substituted in the $\text{C}_6\text{H}_2\text{Me}_3$ by Cl_2 , but with SOCl_2 and $\text{Br}\cdot\text{CHCl}_3$ give mesityl α -chloro-, m.p. 134° , and -bromo- $\beta\beta$ -diphenylvinyl ketone, m.p. 152° , which are as reactive as CPh_2Hal ; they yield the corresponding methoxy-, m.p. 60° , and ethoxy-ketone, m.p. 121° , and with metals, e.g., Hg, give $\gamma\delta\delta$ -tetraphenyl- $\alpha\alpha$ -dimesitylhexa- $\alpha\beta\epsilon\zeta$ -tetraone, m.p. 194° , also obtained from the enol (VI) by FeCl_3 . $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ is hydrogenated ($\text{Pd}\cdot\text{CaCO}_3$; less well, Pt) in EtOAc to a solution, which gives 10-12% of peroxide, this being the min. amount of enol present, but, when reduction is effected by $\text{Zn}\cdot\text{AcOH}$, the yield of peroxide is 90%. R. S. C.

Biochemistry of micro-organisms. LIV. Molecular constitution of terrein, a metabolic product of *Aspergillus terreus*, Thom. P. W. CLUTTERBUCK, H. RAISTRICK, and F. REUTER (Biochem. J., 1937, 31, 987-1002).—Terrein (I), $\text{C}_8\text{H}_{10}\text{O}_3$, m.p. 127° , $[\alpha]_{\text{D}}^{20} + 185^\circ$ in H_2O , is a colourless, powerfully reducing substance containing 1.39 active H atoms at 18° and 2.06 at 28° (in $\text{C}_5\text{H}_5\text{N}$), giving a *p*-bromobenzoate, m.p. $145-146^\circ$, a mono-, m.p. 211° , and a bis-2:4-dinitrophenylhydrazone, m.p. $>360^\circ$, one CO group, titrating with $\text{NH}_2\text{OH}\cdot\text{HCl}$, being present as $\text{CO}\cdot\text{CH}(\text{OH})$. (I) with $\text{Pd}\cdot\text{C}\cdot\text{H}_2$ rapidly absorbs 2 H_2 giving tetrahydroterrein (II), m.p. 84° , $[\alpha]_{\text{D}}^{20} - 280^\circ$ in H_2O , which when warmed with dil. H_2SO_4 loses H_2O , giving 2-keto-4-propylcyclopentanone (III) (3:5-dinitrobenzoate, m.p. 116° ; bis-2:4-dinitrophenylhydrazone, m.p. 241°). The latter was synthesised for comparison. (II) when treated with 3:5-dinitrobenzoyl chloride and with 2:4-dinitrophenylhydrazine hydrochloride gave the same two compounds respectively, H_2O being lost during their formation. (II) on distillation loses H_2O and gives a small amount of (III) together with a large yield of 3-keto-4-propylcyclopentanone, the mixture with $\text{Pd}\cdot\text{C}\cdot\text{H}_2$ giving a mixture of 2-hydroxy- (IV) and 3-hydroxy-4-propylcyclopentanone (V). Both (I) and (II) on exhaustive reduction with $\text{Pd}\cdot\text{C}\cdot\text{H}_2$ give a mixture of (IV) and (V), the latter having m.p. 124° (dinitrophenylhydrazone, m.p. 196° ; semicarbazone, m.p. 157°). (II) with HIO_4 gives an aldehydo-acid, $\text{C}_7\text{H}_{12}\text{O}_3$ [dinitrophenylhydrazone, m.p. 157° (*Et* ester m.p. 86°)], which with alkaline I gives *d*-*n*-propylsuccinic acid, m.p. 103° , $[\alpha]_{\text{D}}^{20} + 26.6^\circ$ in H_2O , which was prepared by resolution of the synthetic *dl*-acid

with strychnine. (I) with HIO_4 gives an *aldehydo-acid*, $\text{C}_7\text{H}_5\text{O}_3$, m.p. 82° , which with $\text{Pd}-\text{C}-\text{H}_2$ gives the lactone of γ -hydroxy- β -propylbutyric acid, b.p. $110-112^\circ/20$ mm. (*phenylhydrazide*, m.p. 115°), which was synthesised for comparison. Decomp. of the ozonide of (I) gives MeCHO . (I) is probably 2-hydroxy-3:5-oxido-4-propenylcyclopentan-1-one.

P. W. C.

Constituents of the adrenal gland. IX. Function of the last oxygen atom. M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 817—827).—Compounds already briefly described (cf. A., 1936, 473, 605, 704, 854, 1382; this vol., 105) are further examined. Hydrogenation of adrenosterone affords the triketone (I), m.p. $178-180^\circ$, identical with the "diketone" obtained from substances A, C, and D (*loc. cit.*) by CrO_3 oxidation. The monoketone (II), m.p. $231-235^\circ$, obtained from substance A by $\text{Pb}(\text{OAc})_4$ or HIO_4 oxidation, is converted by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ into a *diacetate*, $\text{C}_{23}\text{H}_{34}\text{O}_5$, m.p. 156° , which reacts with Girard's reagent, and is therefore not the Ac derivative of the enolic form of a CO group in position 17. Under milder conditions (II) is converted into a *monoacetate*, $\text{C}_{21}\text{H}_{32}\text{O}_4$, m.p. $230-231^\circ$, which with CrO_3 in AcOH affords 11- or 12-ketotrans-androsterone acetate, hydrolysed by $\text{KOH}-\text{MeOH}$ to 11- or 12-ketotrans-androsterone, m.p. $166.5-168^\circ$. This with CrO_3 affords (I), hydrogenated by (H_2 , Raney Ni) to a *diol* (III), $\text{C}_{19}\text{H}_{30}\text{O}_3$, m.p. $247-248^\circ$; the *diacetate*, m.p. $162-163^\circ$, is not affected by CrO_3 at room temp., whereas (III) affords (I), and it is concluded that the 11- or 12-CO is not reduced in the prep. of (III). Removal of 2 H_2O from (III) by way of the xanthate affords an unsaturated ketone, m.p. $72-74^\circ$, hydrogenated to *androstane-11(or 12)-one*, m.p. $50-52^\circ$; it is not affected by CrO_3 at room temp. and does not give a semicarbazone. Androstane-3:17-diol is readily converted by the xanthate method, followed by hydrogenation, into androstane.

P. G. C.

$\Delta^3:5$ -Androstadiene-17-one.—See A., III, 321.

Syntheses of $\alpha\beta$ -dicinnamoylthane and its *pp'*-dimethoxy-derivative. J. ŚWIDERSKI (Rocz. Chem., 1937, 17, 226—232).— Et_2 sodiomalonate and cinnamoyl chloride in Et_2O yield *Et*₂ cinnamoylmalonate, m.p. 26° (Cu salt, m.p. 217°). *Et* cinnamoylacetate is converted by treatment successively with Na and I into *Et*₂ $\alpha\beta$ -dicinnamoylsuccinate, m.p. 96° , from which $\alpha\beta$ -dicinnamoylthane (I), m.p. 130° [*diphenylhydrazone*, m.p. 197° (decomp.)], is prepared by autoclaving (10 atm.: 4 hr.). *Et*₂ *p*-methoxycinnamoylmalonate, m.p. 60° (Cu salt, m.p. $201-202^\circ$), $\alpha\beta$ -di-*p*-methoxycinnamoylthane (II), m.p. 156° [*diphenylhydrazone*, m.p. 200° (decomp.)], and *Et*₂ $\alpha\beta$ -di-*p*-methoxycinnamoylsuccinate, m.p. $138-139^\circ$, have been prepared analogously. (I) and (II) differ from $\text{CH}_2(\text{CO}\cdot\text{CH}\cdot\text{CHPh})_2$ in having only a faint yellow colour, in not being substantive dyes for cotton, and in not giving colour reactions with FeCl_3 .

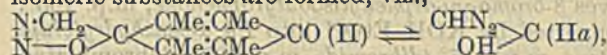
R. T.

Synthesis of $\alpha\beta$ -di-(3:4-methylenedioxy-cinnamoyl)ethane. W. LAMPE and J. POHOSKA (Rocz. Chem., 1937, 17, 233—236).—3:4-Methylenedioxy-cinnamoyl chloride and Me sodioacetoacetate in Et_2O , at the b.p., yield Me α -3:4-methylenedioxy-cinn-

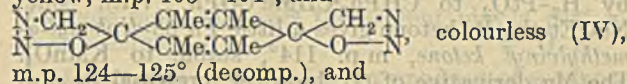
amoylacetate, m.p. $96-98^\circ$, converted by aq. NH_3 into Me 3:4-methylenedioxy-cinnamoylacetate. 3:4-Methylenedioxy-cinnamoylacetone when treated successively with Na and I yields $\alpha\beta$ -di-(3:4-methylenedioxy-cinnamoyl)- $\alpha\beta$ -diacetylthane, m.p. $200-202^\circ$, and this gives $\alpha\beta$ -di-(3:4-methylenedioxy-cinnamoyl)-ethane (I), m.p. $199-200^\circ$, when boiled with aq. AcOH . (I) is a yellow substantive dye for cotton, and gives a colour reaction with FeCl_3 .

R. T.

Action of diazomethane on duroquinone. L. I. SMITH and W. B. PINGS (J. Org. Chem., 1937, 2, 95—111).— CH_2N_2 probably reacts with the CO of duroquinone (I); reaction with the C:C of (I) and reaction of (I) as 4-hydroxy-2-methylene-3:5:6-trimethyl- $\Delta^3:5$ -cyclohexadien-1-one are both excluded by the nature of the products. Structures assigned below, particularly (IV) and (V), are, however, uncertain, tautomeric variations being possible, although less probable. Reaction of CH_2N_2 and (I) is variable, except in MeOH ; in general, two pairs of isomeric substances are formed, viz.,



an unstable oil, and $\begin{array}{c} \text{N}=\text{N} \\ | \\ \text{CH}_2-\text{O} \end{array} > \text{C} < \begin{array}{c} \text{CMe}:\text{CMe} \\ \text{CMe}:\text{CMe} \end{array} > \text{CO} \text{ (III)},$ yellow, m.p. $103-104^\circ$, and



m.p. $124-125^\circ$ (decomp.), and $\begin{array}{c} \text{N}=\text{N} \\ | \\ \text{CH}_2-\text{O} \end{array} > \text{C} < \begin{array}{c} \text{CMe}:\text{CMe} \\ \text{CMe}:\text{CMe} \end{array} > \text{C} < \begin{array}{c} \text{CH}_2-\text{N} \\ | \\ \text{O} \end{array} > \text{N} \text{ (V)}, \text{ m.p. } 143-144^\circ \text{ (decomp.)}.$

Further reaction of (II) or (III) with CH_2N_2 gives (V), proving the mixed $\alpha\beta$ - $\beta\beta'$ -furodiazoline nature of (V). With FeCl_3 , KMnO_4 , Br, or $\text{Ac}_2\text{O}-\text{NaOAc}$ (II) gives (I) and with $\text{Zn}-\text{Ac}_2\text{O}-\text{NaOAc}$ duroquinol diacetate, as sole isolable products. When heated, (II) readily gives (?) 2:3:5:6-tetramethyl- $\Delta^2:5$ -cycloheptadiene-1:4-dione, m.p. $60-61^\circ$ [*dioxime*, m.p. $241-242^\circ$ (decomp. from 220°); no phenyl- or *p*-nitrophenyl-hydrazone], stable to Ac_2O , HCl , H_2SO_4 , CrO_3 , and dil. HNO_3 , and giving with KMnO_4 and O_3 only traces of oily products. The instability of (II) is held to be due to its reaction as (IIa). Even boiling, however, has no effect on (III); it cannot be sublimed, is odourless, gives (I) with FeCl_3 or, by an obscure mechanism, with Ac_2O followed by NaHCO_3 ; with NH_2OH it gives (?) an impure *oxime*, m.p. $201-203^\circ$ (decomp.), with $\text{Br}-\text{CHCl}_3$ a substance (C 47.2, H 4.8, N 9.5%), m.p. $83-84^\circ$, with $\text{Zn}-\text{AcOH}$ a product, m.p. $250-256^\circ$ or $198-200^\circ$ (decomp.) [the latter giving an (?) Ac derivative, m.p. $130-138^\circ$, and indefinite results with FeCl_3], and with SnCl_2 affords a N-free substance, m.p. $213-215^\circ$, which with FeCl_3 gives (I). In boiling PhCl (IV) gives 2 mols. of N_2 and (?) 2:3:6:7-tetramethyl- $\Delta^2:6$ -cyclooctadiene-1:4- or -1:5-dione, m.p. $143-144^\circ$ [*dioxime*, m.p. $>260^\circ$ (decomp. from 250°); no phenylhydrazone]. 1- $\text{C}_{10}\text{H}_7\cdot\text{CNO}$ has no action on (IV), but PhNCO yielded in one experiment (V) and in another a (?) phenylurethane (VI), m.p. $160-161^\circ$, and a substance (C 67.5, H 5.4, N 14.7%), m.p. $127-128^\circ$ (decomp.); with NH_2OH (IV) gives only a red oil, with $\text{NHPh}\cdot\text{NH}_2$ a (?) phenylhydrazone, $\text{C}_{18}\text{H}_{22}\text{ON}_6$, m.p. $144-145^\circ$ (decomp.), with Ac_2O

and a drop of H_2SO_4 a diacetate, $\text{C}_{16}\text{H}_{20}\text{O}_4\text{N}_4$, m.p. $>260^\circ$, with AgNO_3 a *Ag* salt (*Ag* 34.5%), m.p. 128–129° (decomp.), with HCl a (?) dihydrochloride, (C 37.5, H 6.3%; mol. wt. 373), m.p. 112–114°, and with HBr a substance, m.p. 155–156° (decomp.), which in Et_2O – EtOH gives a (?) dihydrobromide (C 39–41, H 6.0–6.1, N 14.5%; mol. wt. 430), m.p. 139–140° (decomp.). Decomp. of the acid salts, which are similarly obtained from (V), by alkali or heat gives only (I), and their nature is obscure. Thermal decomp. of (V) at 155–180° gives only 1 mol. of N_2 and two unstable isomeric substances, $\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_2$, m.p. 103–113° and 125–129°, respectively, giving the same unstable (?) *Ac* derivative, m.p. 138–143°, and of which one may be

$\text{CH}_2\text{O} \cdot \text{C} \begin{matrix} \text{CMe} \cdot \text{CMe} \cdot \text{CO} \\ \text{N}=\text{N} > \text{C} < \text{CMe} \cdot \text{CMe} \cdot \text{CH}_2 \end{matrix}$; the substance, m.p. 103–113°, gives no oxime, but with Zn –aq. AcOH yields its isomeride. No reaction occurs between (V) and 2 : 4– $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{NH}\cdot\text{NH}_2$, NH_2OH , or semicarbazide; KCNO – AcOH gives a (?) carbamide (C 49.5, H 5.6, N 24.2%), m.p. 251° (decomp. from 245°); Me_2SO_4 – NaOH destroys (V); PhNCO gives (VI); KMnO_4 gives AcOH ; NaOI gives substances (C 63.6, H 7.9, N 24.8%), m.p. 144–145° and (C 49.9, H 5.95, N 21.5%) 107–108°; NH_2Ph in AcOH gives (I) as sole recognisable product; AgNO_3 gives a *Ag* salt (C 25.4–26.6, H 3.5–4.4, N 16.8, *Ag* 34.1–35.2%). The nature of both *Ag* salts is obscure. R. S. C.

New synthesis of 3-acetamido- β -naphthaquinone. H. GOLDSTEIN and P. GARDIOL (Helv. Chim. Acta, 1937, 20, 647–650).—2 : 3– $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$ in NaOH solution with NaNO_2 and H_2SO_4 affords 1-nitroso-3-acetamido-2-naphthol (I), m.p. 193° (decomp.), converted by SnCl_2 – HCl into 1-amino-3-acetamido-2-naphthol, isolated as the hydrochloride; oxidation of the latter with $\text{H}_2\text{Cr}_2\text{O}_7$ affords 3-acetamido- β -naphthaquinone, identical with that prepared from β -naphthaquinone by nitration etc. (cf. A., 1892, 1229); treatment with NH_2OH affords (I).

P. G. C.

Magnesium derivative of pinene hydrochloride. Action of phthalic anhydride followed by magnesium ethyl bromide. R. BOUSSET (Bull. Soc. chim., 1937, [v], 4, 368–370).—Pinene hydrochloride with Mg – Et_2O yields its Mg derivative, which when condensed with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ and then treated with MgEtBr – Et_2O , all in an atm. of H_2 , yields a product separated into an acid and a neutral fraction. The crude acid has m.p. 250–258° and resinifies in a few hr. From the neutral fraction bornylene and a compound, m.p. 193.5°, $[\alpha]_D +16.66^\circ$, $[\alpha]_V +17.5^\circ$, $[\alpha]_B +25^\circ$, have been isolated. The latter is unsaponifiable, does not form an oxime or semicarbazone or contain a reactive H (Zerevitinov).

H. G. M.

Camphor series. IV. Synthesis of thiofenchone and two isomeric bis-thiocamphors and their derivatives. D. C. SEN (J. Indian Chem. Soc., 1937, 14, 214–218).—Fenchone (I) in EtOH with H_2S – HCl affords thiofenchone (II) [which gives the oxime and semicarbazone of (I)], reduced by Al – Hg in moist Et_2O to thiofenchol, b.p. 95°/5 mm., 216–220°/762 mm.; this decolorises Br , I , and dil.

aq. KMnO_4 . *l*–(III) and *dl*–Thiocamphor with NaNH_2 in hot C_6H_6 afford, respectively, 1-bis-thiocamphor (IV), m.p. 180°, $[\text{M}]_D^{20} -1109.5^\circ$ in C_6H_6 [dioxime, m.p. 197°; azine, m.p. 200° (decomp.)]; azine picrate, m.p. 200° (decomp.), and *dl*–bis-thiocamphor (V), m.p. 164° (dioxime, m.p. 199°; azine, m.p. 176°); these derivatives are of the corresponding bis-camphors, and their formation shows that (IV) and (V) contain CS groups and are not disulphides. Al – Hg in moist Et_2O converts (V) into *dl*–bis-thioborneol, m.p. 143°. In C_6H_6 (II), (III), and (IV) show an absorption band between 5270 and 4530 Å. with centre at 4950 Å.

P. G. C.

Pyrolysis of myrtenyl selenide. G. DUPONT, K. SEAWINSKI, and W. ZACHAREWICZ (Rocz. Chem., 1937, 17, 154–160).—The same acids (norpinic and nopinic) are obtained by KMnO_4 oxidation of the products of pyrolysis (140–150°/15 mm.) of the non-volatile selenides obtained by oxidising pinene with SeO_2 and of myrtenyl selenide. The latter pyrolyses mainly to verbenene, which with H_2Se gives nopinene.

R. T.

Sesquicryptol, a new crystalline sesquiterpene alcohol in the essential oil of Japanese sugi (Cryptomeria japonica, Don) leaves. S. UCHIDA and S. MURATA (J. Soc. Chem. Ind. Japan, 1937, 40, 159B).—Oil of sugi leaves yields 1% of a sesquiterpene alcohol, $\text{C}_{15}\text{H}_{26}\text{O}$, b.p. 172–174°/20 mm., m.p. 49–51°, $[\alpha]_D^{25} +22.72$ in CHCl_3 (tetrahydride; dihydrochloride; acetate; *H* phthalate), for which the name “sesquicryptol” is proposed. When oxidised (H_2CrO_4), it yields an aldehyde, and with P_2O_5 , a sesquiterpene, $\text{C}_{15}\text{H}_{24}$, b.p. 250–255°/760 mm., which yields a dibromide, and with S or Se a liquid hydrocarbon.

J. D. R.

Biogenesis of the terpenes. K. GANAPATHI (Current Sci., 1937, 6, 19–20).—From a consideration of the distribution of the terpenes, it is suggested that the precursor of many of them is linalool, and a scheme of derivation is formulated.

F. R. S.

Polymerisation of terpenes. M. O. CARMODY and W. H. CARMODY (J. Amer. Chem. Soc., 1937, 59, 1312).—Pinene, dipentene, and cedarwood oil are polymerised (75%) by AlCl_3 in C_6H_6 , PhMe , xylene, or hexane at 10°, the whole of the solvent being recovered unchanged.

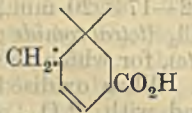
A. Li.

Constitution of shonanic acid, one of the two characteristic volatile acids from the wood of Libocedrus formosana, Florin. IV. Dihydroshonanil alcohol and the optical activity of shonanic acid and its derivatives. V. Oxidation of dihydroshonanil alcohol and the ozonolysis of shonanic acid. VI. Oxidation of dihydroshonanic acid with ozone and potassium permanganate. N. ICHAKAWA (Bull. Chem. Soc. Japan, 1937, 12, 253–257, 258–266, 267–275; cf. this vol., 108).—IV. Reduction (Na – EtOH) of Et , $[\alpha]_D^{25} -4.24^\circ$, or *Ph shonamate*, b.p. 153–155°/6 mm., $[\alpha]_D^{25} -2.40^\circ$, affords dihydroshonanil alcohol. (I), b.p. 104°/7 mm., 228–230°/765 mm., $[\alpha]_D^{25} -2.24^\circ$ (*H* phthalate, m.p. 124°), oxidised (CrO_3 – AcOH) to a mixture of dihydroshonanilaldehyde, b.p. 107–110°/18 mm. (semicarbazone, m.p. 149–150°), and dihydroshonanic acid (II), b.p. 132°/5 mm., whilst hydrogen-

ation (Pd) gives *tetrahydroshonanyl alcohol*, b.p. 100—101°/7 mm., $[\alpha]_D^{25} -1.64^\circ$, also obtained by reduction (Na-EtOH) of Et tetrahydroshonanate. Dehydration (H_3PO_4 ; 200—210°; 1 hr.) of (I) affords *dihydroshonanene*, b.p. 168—169°/759 mm., $[\alpha]_D 0$, and interaction with PCl_5 affords *dihydroshonanyl chloride*, b.p. 87°/13 mm., $[\alpha]_D^{25} -2.00^\circ$, and a compound, b.p. 174°/757 mm.

V. Oxidation ($KMnO_4$ -aq. NaOH) of (I) yields $AcOH$, $H_2C_2O_4$, α -dimethylsuccinic (III) and α -dimethylglutaric acids (IV). Ozonolysis of shonanic acid (V) gives a *mono-ozonide*, m.p. 82° (decomp.), which with H_2O at 75° affords an unsaturated aldehydic acid, $C_6H_{14}O_3$ (?), oxidised (H_2O_2 -aq. NaOH) to an acid, $C_7H_{12}(CO_2H)_2$ (?), the *Me* ester, b.p. 138—140°/7 mm., of which gives an *ozonide*, decomp. on removal of solvent, affording CO_2 , CH_2O , HCO_2H , and an acid, which with HNO_3 (*d* 1.12) (5 hr.; 100°) gives (III) and (IV).

VI. Mild oxidation ($KMnO_4$ -1% aq. NaOH) of (II) affords a dibasic ketonic acid, $C_{10}H_{16}O_5$ (VI) (*Et*₂ ester, b.p. 276°/758 mm., $[\alpha]_D^{25} -1.08^\circ$), and *dihydroxydihydroshonanic acid*, m.p. 161—161.5° [converted into (VI) by $Pb(OAc)_4$ followed by H_2O_2 -aq. NaOH]. (VI) with aq. NaOCl affords a tribasic acid, $C_8H_{12}O_6$ (*Et*₃ ester, b.p. 135—149°/5 mm.), which is converted into (IV) by conc. HCl (0.5 hr.; 100°). Ozonolysis of (II) affords an *ozonide*, which with HNO_3 (*d* 1.12) (2 hr.; 100°) gives a dibasic ketonic acid, $C_8H_{12}O_5$ (*Et*₂ ester, b.p. 138—140°/6 mm., $[\alpha]_D 0$), oxidised (H_2O_2) to (IV). The conclusion reached is that (II) has the annexed structure. F. N. W.



Hydroxytriterpene acids from Somali incense.

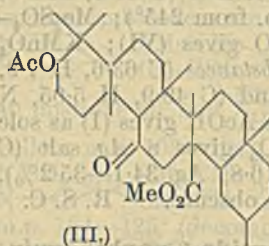
I. F. TROST (Annali Chim. Appl., 1937, 27, 178—188).—The mixed acids, separated as Ba salts and fractionated with Ac_2O , followed by hydrolysis ($EtOH-KOH$) of the fractions, afford α - and β -boswellic acids (Winterstein and Stein, A., 1932, 856) and a third isomeride, γ -boswellic acid, $[\alpha]_D^{25} +279^\circ$. The β -acid is an α -hydroxy-acid, oxidation (CrO_3) yielding the corresponding aldehyde, $C_{28}H_{45}CHO$, m.p. 200—202°, $[\alpha]_D^{25} +127^\circ$ (*oxime*, m.p. 196—197°), whilst the *Me* ester yields the *Me* ester, m.p. 155—157° (*oxime*, m.p. 194—196°), of the keto-acid. High-vac. distillation of α -, β -, and γ -boswellic acids gives α -, β -, and γ -boswelliols, m.p. 114—115°, 139—140°, 115—116°, $[\alpha]_D^{25} +180^\circ$, $+329^\circ$, $+159^\circ$, respectively, the α - having two reactive double linkings and the β - and γ -hydrocarbon onereactive and one difficultly reactive double linkings. All m.p. are corr., all rotations 1% in $CHCl_3$.

F. O. H.

Polyterpenes and polyterpenoids. CXII. Dehydrogenation in the amyryn group. L. RUZICKA, H. SCHELLENBERG, and M. W. GOLDBERG. CXIII. Oxidations in the oleanolic acid group without fission of the ring system. Nature of the fourth oxygen atom of glycyrrhetic acid. L. RUZICKA and S. L. COHEN (Helv. Chim. Acta, 1937, 20, 791—804, 804—808).—CXII. Se dehydrogenation of a mixture of α - and β -amyryn at 350° affords 1:2:3:4- $C_6H_2Me_4$, 2:7- $C_{10}H_6Me_2$, sapotalin (I), 1:2:5:6-

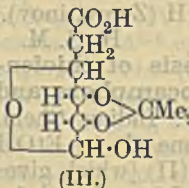
$C_{10}H_4Me_4$ (II), 1:5:6:2- $C_{10}H_4Me_3OH$, a *picene* homologue, $C_{25}H_{20}$, m.p. 302—304°, and a *hydroxy-picene homologue*, $C_{24}H_{18}O$ or $C_{25}H_{20}O$, m.p. 331—332° (*Me ether*, m.p. 358—359°). β -Amyronesemicarbazone with NaOEt affords β -amyrene, m.p. 162—163°, $[\alpha]_D +50.7^\circ$ in $CHCl_3$, which with Se at 340° is converted into 2:7- $C_{10}H_6Me_2$, 1:2:5- $C_{10}H_5Me_3$ (I), and two substances, $C_{30}H_{52}$ (amyrane?), m.p. 226—227°, and $C_{25}H_{20}$ or $C_{24}H_{18}$, m.p. 304—305°; the latter does not depress the m.p. of the substance of m.p. 305—306° obtained from hederagenin or gypsogenin. α -Amyrone with $MeMgI$ affords two substances, probably mixtures of stereoisomeric *methyl-amyryns*, m.p. 225—235° and 198—201°. The former with Se at 340—350° affords (I), (II), and a mixture probably containing chrysene and picene homologues. It is suggested that the formation of $C_{10}H_4Me_4$ is due to the elimination of H_2O and wandering of Me in the amyryns during the reaction with Se.

CXIII. Acetyloleanolic acid is converted by CrO_3 in $AcOH$ into acetylketo-oleanolic lactone, m.p. 282—284°; the *Me* ester with H_2O_2 - $AcOH$ (or CrO_3 ; cf. A., 1934, 412) affords a substance, probably *Me acetylketodihydro-oleanolate* (III), m.p. 195—196°, $[\alpha]_D -10^\circ$ in $CHCl_3$; the corresponding acid has m.p. 195—197°. Use of Bz_2O_2 in place of H_2O_2 affords an isomeride of (III), m.p. 201—204°, which does not possess the absorption band at 2900 Å. ascribed to the CO group in (III). From a comparison of the absorption spectra of these substances it is suggested that glycyrrhetic acid is isomeric with keto-oleanolic acid. P. G. C.



Configuration of shikimic acid, and its degradation to glucodesonic acid. H. O. L. FISCHER and G. DANGSCHAT (Helv. Chim. Acta, 1937, 20, 705—716).—*Me isopropylideneshikimate* is converted into its *Ac* derivative, m.p. 76—77°, which with $KMnO_4$ affords *Me* 1:4:5:6-tetrahydroxy-3-acetoxy-4:5-isopropylidenehexahydrobenzoate, m.p. 135°; this is converted by $Ac_2O-C_5H_5N$ into *Me* 4:5-dihydroxy-1:3:6-triacetoxy-4:5-isopropylidenehexahydrobenzoate, m.p. 121—122°, and by 2*N*-NaOH at room temp. followed by HIO_4 and then NaOBr, into $\alpha\beta\gamma$ -tri-hydroxy- $\alpha\beta$ -isopropylideneadipic lactone (I), m.p. 129—130° [*Me* ester (II), m.p. 84—85°, and its *amide*, m.p. 122° (decomp.)]. (I) with 50% $AcOH$ affords $\alpha\beta\gamma$ -tri-hydroxyadipic dilactone, m.p. 141—143°, converted by $NHPh-NH_2$ into $\alpha\beta\gamma$ -trihydroxyadipic diphenylhydrazide, m.p. 206° (decomp.). (II) with $MeMgI$ affords

$\beta\gamma\delta\epsilon$ -pentahydroxy- $\gamma\delta$ -isopropylidene- $\beta\eta$ -dimethyloctane, m.p. 143—144°, converted by $AcOH$ into $\beta\gamma\delta\epsilon\eta$ -pentahydroxy- $\beta\eta$ -dimethyloctane, m.p. 108—109°. If, in the prep. of (I), $Br-AcOH$ is used in place of NaOBr, the cyclic form of $\beta\gamma\delta$ -trihydroxy- $\gamma\delta$ -isopropylideneadipic semialdehyde (III), m.p. 154° (acetyl nitrile, m.p. 112°), is obtained. (III) with $AcOH$ affords



γδ-trihydroxyadipic semialdehyde lactone (IV), m.p. 176° (decomp.) [*phenylhydrazone*, m.p. 154° (decomp.); *benzylphenylhydrazone*, m.p. 154—160° (decomp.)]. Reduction of (IV) (Ni) affords glucodesonic lactone, and this, its phenylhydrazone, and Me₃ ether are identical in m.p., mixed m.p., and [α]_D with the corresponding substances prepared from glucose. This fixes the structure of shikimic acid as 3 : 4 : 5-trihydroxy-2 : 3 : 4 : 5-tetrahydrobenzoic acid, and the spatial configuration of the OH at 3, 4, and 5 as the same as those at 3, 4, and 5 in *d*-glucose. The intermediate stage in the prep. of (I) is *α-keto-γδ-trihydroxy-δε-isopropylideneheptonic acid semialdehyde* [dinitrophenylhydrazone, m.p. 144° (decomp.); *p-nitrophenylhydrazone*, m.p. 180° (decomp.)]. P. G. C.

Crystalline components of Cortex Simaruba Amara. O. GLEMSER and E. OTT (Ber., 1937, 70, [B], 1513—1519).—Treatment of the bark with H₂O at 80—90°, concn. of the aq. extract, and treatment with CHCl₃ affords simarubin (I), C₂₂H₃₀O₈, m.p. 230—231, [α]_D²⁵ + 59.88° in MeOH, the tasteless simarubidin (II), C₂₂H₃₂O₈, m.p. 260°, [α]_D²⁵ + 48.1° in C₅H₅N, and a non-identified substance, m.p. 243—245°, [α]_D¹⁷ + 14.0° in C₅H₅N. (I) is transformed by Ac₂O-C₅H₅N at room temp. into the *penta-acetate*, m.p. 169—170°, [α]_D¹⁷ + 41.22° in C₅H₅N, whereas at 100° the *anhydro-penta-acetate*, m.p. 180°, is produced. (I) reduces hot Fehling's solution and gives a *phenylhydrazone*, m.p. 204° (decomp.) after softening at 161°, but a semicarbazone could not be prepared. With CH₂N₂ in Et₂O (I) yields a Me₁ ether, m.p. 280°, [α]_D¹⁵ - 65.97° in C₅H₅N. (I) therefore contains 5 OH of which one is phenolic but does not react with FeCl₃. (I) rapidly decolorises aq. KMnO₄. Treatment of (I) with 2% or 5% HCl gives, in place of the expected hexose, a compound, m.p. 228° (decomp.), [α]_D¹⁷ + 64.74°, mol. wt. 400 [*phenylhydrazone*, m.p. 139—140° (decomp.) after softening at 125°]. Oxidation of (I) by CrO₃ in AcOH + KHSO₄ gives *simarubaic acid*, C₁₂H₁₆O₈, m.p. 160° after softening at 143°, whilst ozonisation in EtOAc affords *simarubic acid*, m.p. 164—166° after softening at 143°, [α]_D¹⁸ + 69.9° in MeOH (*phenylhydrazone*, m.p. 174—175°). Treatment of (I) with red P and HI (*d* 1.7) at 280° gives a fluorescent oil, b.p. 120—180°/40 mm. (II) yields a *penta-acetate*, m.p. 122°, and gives Selivanov's reaction for hexoses. Catalytic hydrogenation (Pd) gives an optically inactive product, m.p. 243°, with a bitter taste. Degradation with HI-red P gives the same products as are obtained with (I). Unlike (I) it does not contain phenolic OH or CO. The function of four of the nine O is unexplained. H. W.

Selenium dehydrogenation of α-tocopherol. C. S. MCARTHUR and E. M. WATSON (Science, 1937, 86, 35).—Dehydrogenation (Se at 300—330°) yields a fluorescent oil and crystals, m.p. 106° (duroquinone?). This probably corresponds with a side-chain, in α-tocopherol, consisting of two isoprene units.

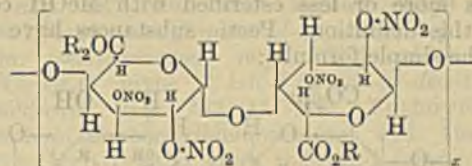
L. S. T.

Determination of the constitution of ammorinol. H. RAUDNTZ (Ber., 1937, 70, [B], 1582—1583).—Oxidation of hexahydroammorinol by cold alkaline KMnO₄ and treatment of the crude product with CH₂N₂ yields an ester which according to analysis

cannot be Me₂ γγλ-trimethyldodecylmalonate postulated by Spath (this vol., 38). When distilled in a high vac. it affords Me γγλ-trimethyltridecoate.

H. W.

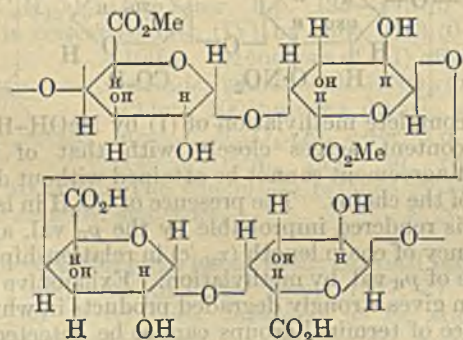
Esterification of pectin substances. IV. Determination of the constitution of pectin esters. G. G. SCHNEIDER and V. FROTSCHI (Ber., 1937, 70, [B], 1611—1617).—Treatment of pectin nitrate (I) with 12% HCl gives HNO₃, MeOH, CO₂, and furfuraldehyde. It is oxidised by HNO₃ (*d* 1.15—1.10) to mucic acid and hydrolysed by non-oxidising acids (1—2%) to galacturonic acid. Since methylated mucic acid is not obtained by the oxidation of (I) and since the acidity of (I) increases as the OMe content decreases it follows that OMe is present in CO₂Me. Complete analyses, particularly determination of CO₂H, and measurement of the mol.-wt. of (I) from various sources show the impossibility of the presence of arabinose and galactose as integral components of (I) and hence of the pectin skeleton. The long pectin chains are formed essentially from galacturonic acid alone and since AcOH is absent the structure of (I) is



After complete methylation of (I) by MeOH-HCl the OMe content agrees closely with that of CO₂H. Perfect agreement cannot be attained without degradation of the chains. The presence of CO₂H in lactonic union is rendered improbable by the *p_H* val. and the constancy of chain length (*η_{sp}/c*) in relationship to the change of *p_H* val. by methylation. Exhaustive esterification gives strongly degraded products in which the presence of terminal groups cannot be detected, thus supporting the evidence of viscosimetric and osmotic methods that long mol. chains are present. H. W.

Constitution of pectin substances. G. G. SCHNEIDER and H. BOCK (Ber., 1937, 70, [B], 1617—1630).—It is proposed to use the term "pectin substances" to describe technical products containing ballast material and "pectin" to denote the corresponding homogeneous materials, i.e., methylated polygalacturonic acids (I). "Pectic acid" denotes the strongly acidic (I) wholly or partly free from OMe whilst "hydropectin" analogously to "hydrocellulose" is the material obtained by partial degradation with acid. Ehrlich's formula is criticised. The conception of a "tetragalacturonic acid" is not in harmony with determinations of mol. wt., and complete methylation and determination of terminal groups show that the polygalacturonic acid contains < 10 galacturonic units. This is also true for pectolic and pectolactonic acid. Further X-ray evidence is against the presence of a "cyclic tetragalacturonic acid" and indicates the presence of extended mols. According to Ehrlich the hydrolysis of "primary pectic acid" proceeds: C₄₁H₆₀O₃₈ + 9H₂O = 4C₆H₁₀O₇ + 2MeOH + 2AcOH + C₅H₁₀O₅ (*l*-arabinose) + C₆H₁₂O₆ (*d*-galactose). In the author's experience, however, it is impossible to obtain a pectic acid from natural

sources which does not have a much higher content of MeOH etc. than that required by this scheme. Treatment with 70% EtOH of pectic acid obtained from citrus, orange, or apple by boiling H₂O removes only the simpler pentosans; this is the reason for the complexity of Ehrlich's formula. A more dil. EtOH removes the more complex pentosans but with increasing purification there is increased divergence from Ehrlich's conception and the analytical vals. approach more closely those required by a highly methylated polygalacturonic acid. There is no fixed relationship between pentosans and pectic acid and there is no reason for involving the pentosans or other hemicelluloses in the formula of pectic substances. Pectin substances can be degraded by decarboxylation to pentosan chains but there is no justification for unnecessarily complicating the pectin formula by inclusion of arabinoses etc. Pectin substances are complex, carbohydrate-like, vegetable materials which have the ability of forming gels with sugars under certain conditions. All substances isolated from fruits which have been found to consist of galacturonic acid chains more or less esterified with MeOH comply with this definition. Pectic substances have therefore the simple formula:



Ehrlich's assumption of the presence of Ac rests on the Ac vals. obtained after hydrolysis with 0.2% NaOH at 100° during 5 hr. With completely purified, authentic products Ac cannot be detected by mild methods (use of *p*-C₆H₄Me·SO₃H in abs. EtOH or with *p*-C₆H₄Me·SO₃H, 2.5% or 5% H₂SO₄). More drastic methods cause decomp. of galacturonic acid with production of HCO₂H. The properties of pectin substances depend (a) on the mol. size which is fundamental for the formation of threads, films and gels, (b) on the degree of esterification of polygalacturonic acid by MeOH which affects the solubility, and (c) on the ballast material such as the pentosans which are invariably present. The peculiar inability of beet pectin to gelatinise is due to its small mol. size. It appears to be much more firmly attached to the cell wall than is fruit pectin so that only a small proportion is extracted by H₂O. H. W.

Bee poison.—See A., III, 341.

Lignin. VII. Nitration and fission of pine wood. H. FRIESE and H. FÜRST (Ber., 1937, 70, [B], 1463—1473).—Treatment of the finely-divided wood with HNO₃—H₂SO₄ results in considerable degradation with production of much material sol. in the nitrating acid. Better results are obtained

by use of HNO₃—AcOH—H₃PO₄ and these are improved when AcOH is replaced by Ac₂O. AcNO₃ in Ac₂O offers no further advantage. The best results are obtained with HNO₃ (*d* 1.52) and cryst. H₃PO₄. With this reagent wood is converted into a NO₂-derivative with retention of structure and avoidance of oxidative degradation; the OH groups are esterified by HNO₃ and the lignin component suffers direct nitration. Under mild conditions hydrolysis and simultaneous fission of the material take place whereby it becomes completely sol. in H₂O. The mechanism of the reaction is not explained but with aid of ultra-filtration it enables a considerable proportion of the material to be isolated as a complex lignin derivative. HNO₃ may act by direct nitration or by addition of NO₂ and OH at a double linking. Catalytic hydrolysis of nitro-wood cannot be effected with NaOMe (Zemplén); the ester-N is retained and production of MeNO₂ is not observed. Ba(OMe)₂ is ineffective even in boiling solution. H. W.

Lignin. VIII. Preparation and sulphonation of lignin from beech wood. H. FRIESE and H. GLASSNER (Ber., 1937, 70, [B], 1473—1477).—The reaction between red beech wood and H₂SO₄—AcOH—Ac₂O proceeds in much the same manner as with pine wood or rye straw, giving α-cellobiose acetate and ligninsulphonic acids isolated as the Ba salts, divided by ultrafiltration into various fractions closely resembling those obtained previously. Analyses of these indicate a fundamental composition C₃₆H₃₇O₁₃ on the assumption that H₂SO₄ behaves additively with introduction of OH and SO₃H. This agrees with Freudenberg's assumption of a fundamental unit C₉H₁₀O₃₋₄. The hypothesis that H₂SO₄ acts by sulphonation leads to less probable conceptions. H. W.

Constituents of *Verbena officinalis*, L. II. Constitution of cornin. B. REICHERT and W. HOFFMANN (Arch. Pharm., 1937, 275, 474—477; cf. A., 1935, 1041).—Cornin gives a Ac₄ or Ac₅ derivative, m.p. 133°, which yields an oxime, m.p. 175—176°, converted by cold Ac₂O into the Ac₅ or Ac₆ oxime, m.p. 184°. As cornin is a reducing agent, it is thus probably an α-keto-alcohol. Ac determinations give indefinite results. R. S. C.

Paprika pigment. X. Citraurin from capsanthin. L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1937, 530, 291—300).—The product C₃₀H₄₀O₂ obtained by the action of KOH—EtOH—H₂ on capsanthin (I) is identified as citraurin. In general, polyenes containing at least 1 CO conjugated with the chromophore do not appear completely stable towards alkali. Chromatographic analysis of (I) in C₆H₆ by CaCO₃ gives two zones probably due to enolisation of (I) favoured by C₆H₆. H. W.

Constituents of ch'an su and the constitution of cinobufagin and cinobufotalin.—See A., III, 341.

Saponins of Chinese drug, San-ch'i, *Aralia bipinnatifida*. T. Q. CHOU and J. H. CHU (Chinese J. Physiol., 1937, 12, 59—66).—The drug contains sucrose, arasaponin-A, C₃₀H₅₂O₁₀, m.p. 195—210°, [α] +23° in EtOH (hepta-acetate, m.p. 256°), and arasaponin-B, C₂₃H₃₈O₁₀, m.p. 190—200°, [α] +8°

in EtOH. Hydrolysis of -A with 3% H_2SO_4 gives *arasapogenin-A*, $\text{C}_{17}\text{H}_{30}\text{O}_5$, m.p. 180—188° (*tetraacetate*, m.p. 140—150°), glucose, a substance, $\text{C}_{24}\text{H}_{43}(\text{?})\text{O}_4$, m.p. 244°, and another substance, m.p. 252°. J. N. A.

Tautomerism of gossypol. A. ZAMISCHLAJEVA (Maslob. Shir. Delo, 1937, No. 2, 9).—The no. of OH in gossypol (I), as determined by the Tschugaev-Zerevitinov method, varies from 3.4 to 8.8, according to the conditions. Solutions of (I) in $\text{C}_5\text{H}_{11}\cdot\text{OH}$ become coloured or turbid after 24 hr., in presence or absence of light or air. This effect is not observed with solutions in xylene. R. T.

Biochemistry of micro-organisms. LV. Molecular constitution of geodin and erdin, two chlorine-containing metabolic products of *Aspergillus terreus*, Thom. I. Constitutional relationship of geodin and erdin. P. W. CLUTTERBUCK, W. KOERBER, and H. RAISTRICK (Biochem. J., 1937, 31, 1089—1092; cf. Raistrick and Smith, A., 1936, 1116).—Methylation (CH_3N_2) of geodin, the *d*-form of a Me_1 ether of *dl*-erdin, and of *dl*-erdin gives products of the same empirical formula but each depresses the m.p. of the other. Methylation (CH_3N_2) of optically inactive dihydrogeodin and dihydroerdin gives a product, $\text{C}_{15}\text{H}_{25}\text{O}_2\text{Cl}_2(\text{OMe})_5$, m.p. 108°, which with dil. NaOH in EtOH loses OMe to give a monobasic acid, $\text{C}_{15}\text{H}_{25}\text{O}_3\text{Cl}_2(\text{OMe})_4$, m.p. 168°. Me_2SO_4 -alkali converts geodin and *dl*-erdin into the same product, m.p. 147°; H_2O is added to each mol., the first becoming inactive and "adding" 4, and the second "adding" 5, OMe. This product loses 1 OMe with dil. NaOH-EtOH, giving a monobasic acid, $\text{C}_{15}\text{H}_{25}\text{O}_3\text{Cl}_2(\text{OMe})_5$, m.p. 163°. Acetylation of geodin, involving addition of H_2O , gives a *tetraacetate*, m.p. 209—210°, whilst acetylation of dihydroerdin to the *triacetate*, m.p. 154°, occurs simply. E. A. H. R.

Action of furfuryl bromide on sodium phenoxide; *o*-furfurylphenol and furfuryl phenyl ether. R. PAUL and H. NORMANT (Compt. rend., 1937, 204, 1482—1484).—Interaction of furfuryl bromide with NaOPh in Et_2O -EtOH gives *furfuryl Ph ether* (I), b.p. 133—135°/13 mm. [hydrogenated (Raney Ni) to *tetrahydrofurfuryl Ph ether*, b.p. 144—145°/17 mm.], and some *o*-furfurylphenol (II), b.p. 151—153°/14 mm. (*phenylurethane*, m.p. 99—100°; *o*-*tetrahydrofurfurylphenol*, b.p. 154—156°/15 mm.). It is improbable that (II) results from rearrangement of (I). Furfuryl, like CH_2Ph , renders Br mobile but its effect is insufficient to cause the production of substituted phenols by the action of bromides on phenoxides in slightly ionising media. H. W.

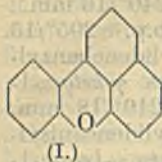
Action of mixed organomagnesium compounds on furyl ketones with two conjugated double linkings. N. MAXIM and (MLE.) M. POPESCU (Bull. Soc. chim., 1937, [v], 4, 265—277).—Furyl ketones ($\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHAr}$; Ar = aryl) with two double linkings react with mixed organo-Mg compounds (MgRX) to give the compounds $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHRAr}$, the double linking attached to Ar being more reactive than that attached to $\text{C}_4\text{H}_3\text{O}$. The resulting compounds with MgRX give saturated $\beta\beta'$ -disubstituted ketones.

Thus difurfurylideneacetone gives the following with the appropriate MgRX : γ -*keto*- α -*di-1-furyl- Δ^a -heptene*, b.p. 199°/20 mm. (*semicarbazone*, m.p. 76°); γ -*keto*- α -*di-1-furyl- Δ^a -octene* (I), m.p. 31°, b.p. 200°/16 mm. (*oxime*, m.p. 90°); γ -*keto*- α -*di-1-furyl- ϵ -phenyl- Δ^a -pentene*, m.p. 102°, b.p. 220—240°/16 mm.; γ -*keto*- α -*di-1-furyl- η -methyl- Δ^a -octene*, b.p. 205°/15 mm. (*semicarbazone*, m.p. 65°). Furfurylidenebenzylideneacetone with $\text{MgPrBr}\cdot\text{Et}_2\text{O}$ gives γ -*keto*- α -1-furyl- ϵ -phenyl- Δ^a -octene, m.p. 33°, b.p. 219°/18 mm. (*semicarbazone*, m.p. 42°), and furfurylideneanisylideneacetone (II) with $\text{MgEtI}\cdot\text{Et}_2\text{O}$ gives γ -*keto*- α -1-furyl- ϵ -anisyl- Δ^a -heptene (III), m.p. 55°, b.p. 241°/22 mm. (*semicarbazone*, m.p. 66°), also obtained by condensing furfuraldehyde with β -*keto*- δ -anisylhexane, b.p. 170°/21 mm. (*semicarbazone*, m.p. 144°), prepared from anisylideneacetone and $\text{MgEtBr}\cdot\text{Et}_2\text{O}$. This establishes the constitution of (III). γ -*Keto*- ϵ -1-furyl- α -anisyl- Δ^a -heptene, b.p. 265°/33 mm. (*semicarbazone*, m.p. 188°), is similarly obtained from β -*keto*- δ -furylhexane. With $\text{MgPrBr}\cdot\text{Et}_2\text{O}$ (II) gives γ -*keto*- α -1-furyl- ϵ -anisyl- Δ^a -octene, b.p. 232°/18 mm. (*semicarbazone*, m.p. 68°), and with $\text{MgBu}^t\text{Cl}\cdot\text{Et}_2\text{O}$ gives γ -*keto*- α -1-furyl- ϵ -anisyl- η -methyl- Δ^a -octene, b.p. 239°/18 mm. (*semicarbazone*, m.p. 163°), which with $\text{MgBu}^t\text{Cl}\cdot\text{Et}_2\text{O}$ gives ζ -*keto*- δ -1-furyl- $\beta\kappa$ -dimethyl-0-anisylundecane, b.p. 242°/17 mm. Furfurylidene-(*p*-dimethylaminobenzylidene)acetone with the appropriate $\text{MgRX}\cdot\text{Et}_2\text{O}$ gives γ -*keto*- α -1-furyl- ϵ -(*p*-dimethylaminophenyl)- Δ^a -heptene, b.p. 253°/13 mm. (*semicarbazone*, m.p. 66°), γ -*keto*- α -1-furyl- ϵ -(*p*-dimethylaminophenyl)- η -methyl- Δ^a -octene, m.p. 59°, b.p. 266°/18 mm. (*semicarbazone*, m.p. 192°), and γ -*keto*- α -1-furyl- ϵ -(*p*-dimethylaminophenyl)-0-methyl- Δ^a -nonene, b.p. 266°/13 mm. (*semicarbazone*, m.p. 60°). With $\text{MgPrBr}\cdot\text{Et}_2\text{O}$ (I) gives ζ -*keto*- δ -*di-1-furyl-undecane*, b.p. 200°/18 mm. H. G. M.

Molecular resonance systems. IV. Absorption spectra of sulphonephthaleins. H. MOHLER, H. FORSTER, and G. SCHWARZENBACH (Helv. Chim. Acta, 1937, 20, 654—658).—If in a compound $\text{XH}_n\cdot\text{T}\cdot\text{XH}_n$ in which T is a sulphonated triphenylcarbonium and XH_n and auxochromic group the H ions are systematically replaced, symmetrical and unsymmetrical compounds are alternately obtained. With fourteen sulphonephthaleins a very close resemblance is found in the absorption spectra of all the symmetrical forms on the one hand and of all the unsymmetrical forms on the other hand. The form of the graphs is discussed. H. W.

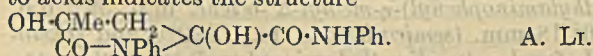
New constituents of coal-tar pitch. O. KRUBER (Ber., 1937, 70, [B], 1556—1564).—Removal of the black pigment from pitch by treatment with naphtha is difficult but by use of superheated steam in a vac. or by distillation at 2—6 mm. > half the material can be volatilised without decomp. A residue, b.p. 395—400°, from the pyrene fraction is freed from acidic (0.5%) and basic (6%) components, treated with Na at 150—155° and then with cold H_2O , and distilled. The main fraction of hydrocarbons thus isolated is a mixture of 2:3- and 1:2-benzofluorene, best separated from one another by use of AcOH. The latter is more readily isolated if the fraction is heated with KOH instead of Na. For the extraction

of compounds containing O, a pyrene residue fraction, b.p. 392—397°, is employed; from this phenylene 2:3-naphthylene oxide (brasan), m.p. 205—206°, is readily isolated after partial oxidation with $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH or by use of molten KOH. The residues



afford 1:9-benzoxanthene [7-oxabenzanthrene] (I), b.p. 395°/758 mm. (picrate, m.p. 124°), reduced (Na and EtOH) to 1:9-tetrahydrobenzoxanthene, b.p. 204—206°/15 mm., m.p. 58°, which is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH at room temp. to β -1-xanthonepropionic acid, m.p. 169—170°; this is further oxidised by KMnO_4 to 1-xanthoneglyoxylic acid (II), m.p. 187—188°, and 1-xanthoneacetic acid, m.p. 176—177°. Treatment of (II) with NaOH –10% H_2O_2 affords xanthone-1-carboxylic acid, m.p. 229—230°, decarboxylated to xanthone. A dihydrobrasan, m.p. 157°, is incidentally described. H. W.

Dimerisation of pyruvic anilide. J. V. SCUDI (J. Amer. Chem. Soc., 1937, 59, 1403—1404).—Treatment of pyruvanilide (I) with NH_4Et in COMe yields a dimeride (II), which reacts with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in cold dil. NaOH giving the oxime of (I), and is hydrolysed by boiling dil. NaOH to NHPh_2 (extracted with Et_2O) and BzCO_2H (pptd. as phenylhydrazine). The formation from (II) of an OEt-derivative, m.p. 198°, with EtOH and HCl, and an Ac derivative, m.p. 148—150°, with conc. H_2SO_4 in boiling Ac_2O shows that (II) is unsymmetrical, whilst its stability to acids indicates the structure



A. Li.

Mechanism of closure of the pyrrole ring in the dry distillation of ammonium mucate. E. S. CHOTINSKI (Trav. Inst. Chim. Charkov, 1935, 1, 19—32).—It is concluded from a review of the lit. that pyrrole and pyrrolecarboxylamide are formed respectively from $(\text{NH}_4)_2$ mucate (I) and NH_4 mucinamate (II), and that conversion of (I) into (II) precedes ring-closure. R. T.

Pyrrole derivatives. V. B. TOI and S. AKABORI (Bull. Chem. Soc. Japan, 1937, 12, 316—318).—The following compounds are obtained by condensing $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ with the appropriate β -aminoaldehyde obtained by the reduction ($\text{Na}\cdot\text{Hg}$, $\text{EtOH}\cdot\text{H}_2\text{O}$, -10°) of the corresponding β -substituted aminoacetic ester: Et 2-methyl-, Et 2:5-dimethyl-, and Et 2-methyl-5-isobutyl-pyrrole-3-carboxylate, m.p. 66.5—67.5°, and β -2-methyl-3-carbethoxy-5-pyrrolpropionic acid, m.p. 176—177°. F. N. W.

N-Arylbarbituric acids. III. J. S. BUCK (J. Amer. Chem. Soc., 1937, 59, 1249—1251).—Nitration of 1-phenyl-5:5-diethylbarbituric acid yields equal quantities of m-, m.p. 189°, and p-nitro-, m.p. 208°, reduced (PtO_2) to m-, m.p. 226° [hydrochloride, m.p. 242° (decomp.)], and p-amino-, m.p. 234° [hydrochloride, m.p. 256° (decomp.)], -phenyl-5:5-diethylbarbituric acid. Acetylation (Ac_2O) of the last two gives the m-, m.p. 285°, and p-NHAc-compound, m.p. 174°, identical with those prepared by condensing m- and p-NHAc- $\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ respectively with $\text{CET}_2(\text{CO}_2\text{Et})_2$, whilst treatment of the

amines with nitrocarbamide in EtOH yields m-, m.p. about 206°, and p-carbamidophenyl-5:5-diethylbarbituric acid, m.p. about 221°. These condense (NaOEt) with $\text{CET}_2(\text{CO}_2\text{Et})_2$ to give m-, m.p. about 345°, and p-phenylene-NN'-bis-(5:5-diethylbarbituric acid), m.p. about 352°. ClCO_2Et and NaOH convert the NH_2 -compounds into the m-, m.p. 242°, and p-carbethoxylamino-compounds, m.p. 203.5°. o-, m-, and p- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ with $\text{CET}_2(\text{CO}_2\text{Et})_2$ afford respectively 1-o-, m.p. 169°, 1-m-, m.p. 152.5°, and 1-p-chlorophenyl-5:5-diethylbarbituric acid, m.p. 181°, the last two identical with those prepared by diazotisation of the NH_2 -compounds. The diazonium salts are converted by boiling 40% H_2SO_4 into the m-, m.p. 222.5°, and p-OH-compounds, m.p. 191°, and couple with appropriate amines or phenols yielding the azo dyes 1-m- and 1-p-(4-aminobenzeneazo)-, -(4-aminonaphthaleneazo)-, -(4-hydroxynaphthaleneazo)-, and -(2-azo- α -naphthol-5-sulphonic acid)-phenyl-5:5-diethylbarbituric acid. o-Acetamidophenylcarbamide, m.p. 188° (decomp.), obtained by reducing o- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ (Adams method) and treating the amine with nitrocarbamide in EtOH, does not condense with $\text{CET}_2(\text{CO}_2\text{Et})_2$. All m.p. are corr. A. Li.

Enol-betaines. Derivatives of 3:5-diketo-piperidine. C. GUSTAFSSON (Ber., 1937, 70, [B], 1591—1598).—Sarcosine Et ester is converted by $\text{CH}_2\text{Cl}\cdot\text{COMe}$ and anhyd. Na_2CO_3 in abs. EtOH into Et methylacetonylaminoacetate, b.p. 95—96°/6 mm., the methiodide, m.p. 131—134° (decomp.), of which is transformed by NaOEt in warm EtOH into the compound, $\text{C}_{28}\text{H}_{41}\text{O}_8\text{N}_4\cdot\text{NaI}$ (I), m.p. 236—239° (decomp.), which with Ag_2O affords 3:5-diketo-1:1-dimethylpiperidiniumbetaine monohydrate (II), m.p. >300° after gradual decomp. at 240°; this passes at 120°/vac. into the anhyd. betaine,

$\text{CH} < \begin{smallmatrix} \text{C}(\text{O})\cdot\text{CH}_2 \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix} > \text{NMe}_2$. Oxidation of (II) with KMnO_4 in dil. HCl gives methyliminodiacetic acid methochloride, m.p. 207—208° (decomp.), also obtained from Et, methyliminodiacetate methiodide, m.p. 118—120°. (II) is converted by aq. NaI into (I) and by SrBr_2 into the compound, $\text{C}_{14}\text{H}_{22}\text{O}_4\text{N}_2\cdot\text{SrBr}_2$, also $+1\text{H}_2\text{O}$. (II) is transformed into the corresponding chloride, m.p. 213—214° (decomp.), and nitrate, m.p. 179—181° (decomp.), and into the abnormal iodide, $\text{C}_{14}\text{H}_{23}\text{O}_4\text{N}_2\cdot\text{I}$, m.p. 209—210° (decomp.). (I) is converted by NaOMe and an excess of MeI in MeOH into 5-keto-3-methoxy-1:1-dimethyl- Δ^3 -piperidinium iodide, m.p. 169—171° (decomp.); the corresponding 3-OEt-compound has m.p. 175—176° (decomp.). (II) in MeOH immediately decolorises Br and in conc. solution 4-bromo-3:5-diketo-1:1-dimethylpiperidinium bromide, m.p. 203—204° (decomp.), is pptd.; if this is neutralised with NaOH, 4-bromo-3:5-diketo-1:1-dimethylpiperidiniumbetaine, m.p. 229—231° (decomp.), is produced. Treatment of (I) with I in presence of NaHCO_3 leads to 4-iodo-3:5-diketo-1:1-dimethylpiperidiniumbetaine, m.p. 213—214° (decomp.). H. W.

Synthesis of new local anaesthetics. II. K. N. GAIND, A. W. KHAN, and J. N. RAY (J. Indian Chem. Soc., 1937, 14, 237—240; cf. this vol., 243).—Esters

of $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$ are heated under pressure with piperidine in C_6H_6 , and the products benzoylated or *p*-nitrobenzoylated to $\text{C}_5\text{H}_{11}\text{N}\cdot\text{CH}_2\cdot\text{CMe}(\text{CO}_2\text{R})\cdot\text{O}\cdot\text{CO}\cdot\text{R}'$. The following new local anæsthetics are described: *Pr*^a β -chloro- α -hydroxyisobutyrate, b.p. 120°/15 mm. *Pr* α -benzoyloxy- β -piperidinoisobutyrate (hydrochloride, m.p. 115°). *Et* α -benzoyloxy- β -piperidinoisobutyrate (hydrochloride, m.p. 128°). *Et* α -*p*-nitrobenzoyloxy- β -piperidinoisobutyrate (hydrochloride, +1COMe₂, m.p. 76°); the free base on reduction affords *Et* α -*p*-aminobenzoyloxy- β -piperidinoisobutyrate hydrochloride, m.p. 102°. *Pr*^b α -hydroxy- β -piperidinoisobutyrate hydrochloride, m.p. 115° (O-Bz derivative hydrochloride, m.p. 156°; O-*p*-nitrobenzoyl derivative hydrochloride, m.p. 61°). Benzyl α -benzoyloxy- β -piperidinoisobutyrate (hydrochloride, m.p. 195—197°). The NaHSO_3 compound of piperidinoacetone with aq. KCN affords α -hydroxy- β -piperidinoisobutyronitrile, which on conversion into the *Et* ester hydrochloride of the acid and treatment with Na_2CO_3 is decomposed. P. G. C.

Hydroxylamine pyridine compounds of bivalent platinum.—See A., I, 475.

Phenoxypyridine. R. R. RENSHAW (J. Amer. Chem. Soc., 1937, 59, 1406—1407).—Errors in an earlier paper (this vol., 165) are corr. A. LI.

Modification of the Guareschi pyridine synthesis. I. N. PALIT (J. Indian Chem. Soc., 1937, 14, 219—224).—In contrast to the results of Guareschi (cf. A., 1898, i, 274), the reaction between PhCHO , $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, $\text{CHMe}\cdot\text{CAc}\cdot\text{CO}_2\text{Et}$, and NH_3 affords only two products, the known $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CHPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$, m.p. 225—226°, and *Et* 6-hydroxy-3-cyano-4-phenyl-6-methyl-2-piperidone-5-carboxylate (I), m.p. 222—223°; the latter is also obtained from $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ (II) and $\text{CHPh}\cdot\text{CAc}\cdot\text{CO}_2\text{Et}$ in presence of a little NHEt_2 . With dil. HCl (I) affords $\text{CH}_2\text{Ac}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and in alkaline solution with Me_2SO_4 gives *Et* 6-hydroxy-2-methoxy-3-cyano-4-phenyl-3 : 5-dimethyl- Δ^1 -tetrahydropyridine-5-carboxylate, m.p. 162°. Ac_2O in $\text{C}_5\text{H}_5\text{N}$ converts (I) into 6-hydroxy-2-acetoxy-4-phenyl-6-methyl- Δ^1 -tetrahydropyridine, m.p. 145—146°, which is insol. in NaOH solution but suffers ring fission by hot aq. NaOH . From (I) and PCl_3 in C_6H_6 , *Et* 2-hydroxy-3-cyano-4-phenyl-6-methyl- $\Delta^{1:5}$ -dihydropyridine-5-carboxylate, m.p. 142°, is obtained (*Me* ether, m.p. 149°). Condensation of (II) with $\text{CHPh}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ in presence of NHEt_2 for 4—5 days affords 6-hydroxy-3 : 5-dicyano-4-phenyl- $\Delta^{3:6}$ -dihydro-2-pyridone (J.C.S., 1920, 117, 1465), whereas the initial product of the reaction is a NHEt_2 salt, m.p. 266—268°.

P. G. C.

Preparation of amino-3-pyridylmethane. H. ERLENMEYER and A. EPPRECHT (Helv. Chim. Acta, 1937, 20, 690—691).—*Et* nicotinate is converted by way of the amide into the nitrile, which with $\text{Cr}(\text{OAc})_2$ affords 3-pyridylmethylamine, isolated as the dihydrochloride, m.p. 224°; picrate, m.p. 193°. P. G. C.

Reducing action of *N*-glucosido- α -dihydronicotinic amide and analogous compounds. P. KARRER and B. H. RINGIER (Helv. Chim. Acta, 1937,

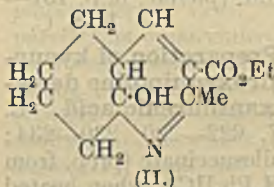
20, 622—625).—Preparative methods are given for the conversion of *N*-*d*-glucosido- α -dihydronicotinamide (I) and its *O*-Ac₁ derivative into *N*-*d*-glucosidopyridinium-3-carboxylamide iodide and its *O*-Ac₄ derivative, respectively. In slightly acid solution (I) reduces 78% of dichlorophenol-indophenol in 1 hr., reduces aq. Ag salts, and converts $\text{o}\text{-C}_6\text{H}_4(\text{NO}_2)_2$ into $\text{o}\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH}$, but in each case more slowly than ascorbic acid. P. G. C.

Manufacture of substituted pyridine- α -dicarboxylic amides.—See B., 1937, 842.

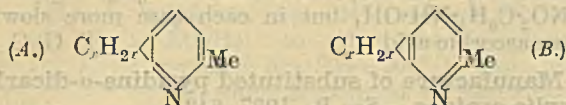
Transformation of indolyl methyl ketones into indole homologues. C. ALBERTI (Gazzetta, 1937, 67, 238—243).—3-Indolyl Me ketone (I) and NaOMe at 210—220° give 3-methylindole and unchanged (I); similarly 2-methyl-3-indolyl Me ketone (II) gives 2 : 3-dimethylindole. With NaOEt, (I) gives 3-ethylindole, and (II) gives 2-methyl-3-ethylindole. Boiling 20—20% H_2SO_4 scarcely attacks (I) or 3-methyl-2-indolyl Me ketone, but converts (II) into 2-methylindole. E. W. W.

Catalytic dehydrogenation of *trans*-decahydroquinoline. J. K. JURIEV and G. I. MIRONENKO (Sci. Rep. Moscow State Univ., 1936, No. 6, 277—279).—Quinoline is obtained in 35% yield from *trans*-decahydroquinoline in presence of C-Pt catalyst at 330°. R. T.

Synthesis of *Bz*-tetrahydroquinolines. III. U. BAST (Annalen, 1937, 530, 131—141; cf. A., 1935, 222).—2-Hydroxymethylenecyclohexanone and $\text{NH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ (I) at -5° give *Et* 10-hydroxy-5 : 6 : 7 : 8 : 9 : 10-hexahydroquinaldine-3-carboxylate (II), m.p. 200—201°, stable at 105°, but dehydrated above the m.p. or by boiling with picric acid in EtOH to *Et* *Bz*-tetrahydroquinaldine-3-carboxylate and simultaneously dehydrated and hydrolysed by boiling 15% KOH. 2-Et oxalocyclohexanone and (I) at 28° give similarly *Et*₂ 10-hydroxy-5 : 6 : 7 : 8 : 9 : 10-hexahydroquinaldine-3 : 4-dicarboxylate, b.p. 191°/5 mm. (picrate, m.p. 134°) (with a small amount of a non-basic, nitrogenous substance, m.p. 212°), and thence the corresponding acid, m.p. 257° (decomp.), which loses CO_2 only with difficulty when heated, but when distilled in vac. with 2 parts of soda-lime gives 10-hydroxy-4 : 6 : 7 : 8 : 9 : 10-hexahydroquinaldine, b.p. 232—234°/754 mm. (picrate, m.p. 191°), partly converted by distillation with PbO into *Bz*-tetrahydroquinaldine. 2-Et oxalo-6-, -5-, and -4-methylcyclohexanone and (I) give similarly *Et*₂ 10-hydroxy-2 : 8-, b.p. 191—192°/12 mm. (picrate, m.p. 144°) (and a substance, m.p. 236°), -2 : 7-, b.p. 206°/12 mm. (picrate, m.p. 87°) (and a substance, m.p. 217°), and -2 : 6-dimethyl-5 : 6 : 7 : 8 : 9 : 10-hexahydroquinoline-3 : 4-dicarboxylate, b.p. 205°/15 mm. (picrate, m.p. 128°) (and a substance, m.p. 230°), the corresponding acids, m.p. 210—211° (decomp.), 238—239° (decomp.), and 236° (decomp.), and 10-hydroxy-2 : 8-, b.p. 241—243°/755 mm. (picrate, m.p. 177°), -2 : 7-, b.p. 248—249°/757 mm. (picrate, m.p. 194—195°), and -2 : 6-



dimethyl-5:6:7:8:9:10-hexahydroquinoline, b.p. 251—253°/754 mm. (*picrate*, m.p. 180—181°), respectively. *Bz-Tetrahydroquinoline* and 6-methyl-2:3-dihydro- β -pyridindene (5:6-trimethylene- α -picoline) derivatives condense with aldehydes to 2-styryl derivatives; this method of distinguishing between formulæ of type (A) and (B) fails, since from



considerations of valency angles (B) should be favoured in the quinoline and (A) in the pyridindene series. The author prefers a centric formula. The following are described, m.p. in parentheses being those of the *hydrochlorides*: *Et* 2-m-, m.p. 141° (170°), and -*p*-nitro-, m.p. 119°, and -*p*-methoxy-, m.p. 96° (173°); *methosulphate*, m.p. 214°, and -*p*-dimethylamino-styryl-*Bz*-tetrahydroquinoline-3-carboxylate, m.p. 120°; 2-*p*-dimethylamino-, m.p. 160°, 2-*p*-, m.p. 203°, and -*m*-nitro-styryl-*Bz*-tetrahydroquinoline, m.p. 217°; 3-acetyl-, m.p. 163—164°, and 3-benzoyl-2-*p*-nitro-styryl-*Bz*-tetrahydroquinoline, m.p. 181—182° (210°); 3-acetyl-2-*p*-nitro-, m.p. 213° (207°), and 2-*p*-methoxy-styryl-6-methyl-*Bz*-tetrahydroquinoline, m.p. 173°; 3-benzoyl-2-*p*-nitrostyryl-6-, *cryst.*, and 7-methyl-*Bz*-tetrahydroquinoline, m.p. 186—187°. 2-Hydroxy-methylenecycloheptanone and (I) at 100° give *Et* 6-methyl-2:3-dihydro- β -pyridindene-7-[5:6-trimethylene- α -picoline-3-]carboxylate, b.p. 178—180°/25 mm. (*picrate*, m.p. 134°; *p*-nitrobenzylidene derivative, m.p. 210°), hydrolysed by 15% KOH to the corresponding acid, m.p. 208° (decomp.), which, when distilled with soda-lime, gives 6-methyl-2:3-dihydro- β -pyridindene [5:6-trimethylene- α -picoline], b.p. 78—80°/20 mm., 195—196°/750 mm. (*picrate*, m.p. 151—152°). R. S. C.

Xanthurenic acid. V. Preparation of kynuronic acid and of other 4-hydroxyquinoline derivatives. VI. Synthesis of xanthurenic acid. L. MUSAJO (*Gazzetta*, 1937, 67, 222—230, 230—234; cf. this vol., 305).—V. Et_2 anilosuccinate (prep. from Et_2 sodio-oxalacetate and $NH_2Ph.HCl$), when heated in petroleum jelly at 280°, yields *Et* kynurenate (*Et* 4-hydroxyquinoline-2-carboxylate); this, and the acid, are identical with products from natural sources. $o-NH_2.C_6H_4.CO_2H$ and $NO_2.CH_2.CH:N.OH$ condense in aq. HCl to form *o*- β -nitroethylideneaminobenzoic acid, m.p. 196° (decomp.) (G.P., 347,375; B., 1922, 522), converted by $NaOAc-Ac_2O$ into 3-nitro-4-hydroxyquinoline, m.p. >300° (*loc. cit.*) (*K* salt; *Bz* derivative, m.p. 144—145°). This is reduced (Sn and HCl) to 3-amino-4-hydroxyquinoline, m.p. >300° (*Bz* derivative, m.p. 289°).

VI. 4-Hydroxy-2-methylquinoline with KOH at 240—300° furnishes xanthurenic acid, m.p. 285° (after purification through the Me ester).

E. W. W.

Synthesis of 2:4-dihydroxyquinoline and its derivatives. Their constitution. P. HEIMANN (*Diss.*, Dijon, 1937, 60 pp.).—The halogenation, nitrosation, and diazonium coupling of 4-hydroxycarbostyryl (I) and its Br-derivatives and a new synthesis of these compounds are described.

Tautomerism between the diphenolic and diketone forms is indicated by the varied modes of reaction. Purification of (I) is readily effected by crystallisation of its *Na* salt. With 1 mol. of Br in cold HCO_2H or with 2 mols. in conc. H_2SO_4 (I) gives the yellow α -(5- or 8-)*Br*-derivative (II), m.p. 199°; with an excess of Br in cold or with 2 mols. in hot HCO_2H it gives the 3-*Br*-derivative (III), m.p. 281°; with 2 mols. of Br in C_6H_6 it gives the 6-*Br*-derivative (IV), m.p. 241° (*NO*-derivative, m.p. 256°). With PBr_5 (I) gives 2:4-*di*-, m.p. 265°, (II) gives 2:4:5- or 2:4:8-*tri*-, m.p. 276°, and (III) gives 2:3:4-*tri*-bromoquinoline, m.p. 288°. PCl_5 converts (II) into 2:4-*dichloro*-5- or -8-, m.p. 174.5°, and (III) into 2:4-*dichloro*-3-bromoquinoline, m.p. 99°. $m-C_6H_4Br.CO_2H$ (modified prep.), b.p. 280°, gives, by way of 5-bromo-2-nitrobenzoyl chloride, m.p. 142°, *Et* 5-bromo-2-nitrobenzoylmalonate, cyclised by Sn-HCl to (IV). $KMnO_4$ oxidises (I) or (II) to 4:6-dihydroxypyridine-2:3-dicarboxylic acid, m.p. 261° (*Ag* and *Pb* salts), which proves that the Br of (II) is in the *Bz* ring; this is confirmed by formation of a *NO*-derivative, m.p. 200°. The orientation of (III) follows from its oxidation to 5-bromo-4:6-dihydroxypyridine-2:3-dicarboxylic acid, m.p. 240° (also obtained from the preceding acid by Br), and from its diazo-synthesis from 3-amino-2:4-dihydroxyquinoline. The *NO*-derivative (V) of (I) crystallises from H_2O at 15° or from $EtOH$ in a yellow, thermolabile form, m.p. 208°, which gives the red form at >100°; from H_2O at >40° it gives a thermostable, yellow monohydrate, m.p. 251°. It gives a green solution of the Na and a reddish-brown solution of the Na_2 salt; by use of <1 NaOH the green, *cryst. Na* salt is isolated, which with $CoCl_2$ gives a brown salt, $Co^{II}(OH)_2.C_9H_5O_3N_2$, converted by HCl into $CoCl_2$, Cl_2 , and a red salt, $Co^{III}(C_9H_5O_3N_2)_2$, also obtained directly from (V) by $CoCl_2$ in $AcOH$; $NiCl_2$ and (V) in $AcOH$, however, give the green salt, $Ni^{II}(C_9H_5O_3N_2)_2$. Me_2SO_4 and (I) give 4-methoxycarbostyryl, m.p. 271.5° (*NO*-derivative, m.p. 220°). *p*- $NO_2.C_6H_4.N_2Cl$ affords 6- and 5-(or 8-)*bromo*-2:4-dihydroxy-3-*p*-nitrobenzeneazoquinoline, m.p. >370°. Diazotised 3-amino-4-hydroxycarbostyryl and (I) give azo-4-hydroxycarbostyryl, m.p. 218°. Long treatment with the appropriate amine converts $CH_2(CO_2R)_2$ into malondi-o-, m.p. 171°, and -*p*-chloroanilide, m.p. 261°, and -*o*-anisidide, m.p. 163°; ethylmalondi-*p*-chloroanilide, m.p. 258°, is similarly obtained; boiling for only 0.5 hr. gives carbomethoxyacet-o-, m.p. 70.5°, and -*p*-chloro-anilide, m.p. 84°, carbomethoxyacet-o-chloroanilide (VI), m.p. 176°, and -*o*-anisidide, m.p. 66°, and α -carbomethoxypropion-*p*-chloroanilide (VII), m.p. 93°. By passing steam into the mono-esters in aq. Na_2CO_3 are obtained malonmono-*p*- (VIII), m.p. 168°, and -*o*-chloroanilide, m.p. 158°, and -*o*-anisidide (IX), m.p. 154°. Addition of $CO_2Et.CH_2.CO.NH.C_6H_4R-p$ ($R = Me$ or Cl) in small portions to paraffin at 250° gives 4-ethoxy-6-methyl-, m.p. 138° [oxidised to 4:6-dihydroxynicotinic acid (*Ag* and *Pb* salts)], and 6-chloro-carbostyryl, m.p. 91°, with a little diamide; $CO_2Et.CH_2.CO.NH.C_6H_4Me-o$ gives only a little 4-ethoxy-8-methylcarbostyryl, m.p. 190°, and much ditoluidide. $CO_2Et.CH_2.CO.NHPh$ and $CO_2Et.CH_2.CO.NH.C_6H_4X-o$ ($X = Cl$ or OMe) give

the diamide and no carbostyryl; (VII) loses EtOH instead of H₂O and yields 5-chloro-4-hydroxycarbostyryl, m.p. 264°, and CO₂Et·CHET·CO·NH·C₆H₄Me-o gives similarly 4-hydroxy-8-methyl-3-ethylcarbostyryl, m.p. 218°. Hot Ac₂O converts *o*- and *p*-C₆H₄Me·NH·CO·CH₂·CO₂Et into *o*- and *p*-C₆H₄Me·NHAc, respectively. PCl₅ converts (VI) and its *p*-analogue into 2:3:8-trichloro-4-ethoxy-, m.p. 63.5° and 4:6-dichloro-2-hydroxy-carbostyryl, m.p. 138°, respectively. P₂O₅ converts the anilido-esters into dianilides. PCl₅ converts the anilido-acids (VIII) and (IX) into 2:3:4:6-tetrachloro-, m.p. 127°, and 2:4-dichloro-8-methoxyquinoline, m.p. 92°, respectively. R. S. C.

Salts and complex derivatives of 4-hydroxy-2:6- and -2:8-dimethylquinoline. A. MEYER and H. DRUTEL (Compt. rend., 1937, 204, 1824—1826; cf. A., 1935, 758, 1506).—The following derivatives of 4-hydroxy-2:6-dimethylquinoline are prepared: *sulphate*, m.p. 240°; *H sulphate*, m.p. 207—208°; *hydrochloride*, m.p. 184—185°; *K derivative*, m.p. 313—315°; *picrate*, m.p. 192°; *picrolonate*, m.p. 230°; *bismuthi-iodide*, m.p. 222° (decomp.); *mercuri-iodide*, m.p. 202°, and *-chloride*; 4-*OMe*- and *-OEt*-derivatives, m.p. 107° (+*MeI*, m.p. 214°; +*EtI*, m.p. 187°) and 75—76° (+*MeI*, m.p. 220°; +*EtI*, m.p. 208—209°), respectively; *ethiodide*, m.p. 208°. The following derivatives of 4-hydroxy-2:8-dimethylquinoline are prepared: *sulphate*, m.p. 222°; *hydrochloride*, m.p. 220°; *picrate*, m.p. 188°; *picrolonate*, m.p. 227—228°; *bismuthi-iodide*, m.p. 217° (decomp.); *mercuri-iodide*, m.p. 180—181° and *-chloride*; 4-*OMe*- and *-OEt*-derivatives, m.p. 103.5° (+*MeI*, m.p. 148—149°) and 77.5° (+*EtI*, m.p. 200°), respectively; *ethiodide*, m.p. 174—175°.

J. L. D.

Production of aldehydes [indoles, carbazoles, quinolines etc.].—See B., 1937, 761.

Dipolar complex salts. A. ABLOV (Bull. Soc. chim., 1937, [v], 4, 1220—1229).—The following substances have been prepared: *Cu quinoline-5-carboxylate* (I), (I)2C₆H₅N, *Ni* and *Co quinoline-5-carboxylate* + 8H₂O, *Cu quinoline-8-sulphonate* + 2H₂O, *Cu tetrapyrindylquinoline-8-sulphonate* (C₆H₅N·SO₃)₂[Cu(C₅H₅N)₄], *Cu quinoline-6-sulphonate* + 6H₂O, (C₆H₅N·SO₃)[Cu(C₅H₅N)₄], (C₆H₅N·SO₃)CuOH + 1.5H₂O (II), and *Cu quinoline-5-sulphonate* + 4H₂O. Acetoxycupric quinoline-5-carboxylate and (II) are probably dipolar complex salts. J. G. A. G.

Tautomerism of ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate. H. V. HEERAMANECK and R. C. SHAH (Proc. Indian Acad. Sci., 1937, 5, A, 442—446).—Et 4-hydroxy-2-phenylquinoline-3-carboxylate (I) (*H sulphate*, m.p. 212—215°; *picrate*, m.p. 247—250°) is shown to react both in the enol and keto-forms. Et 2-phenyl-3-methyl-3:4-dihydroquinoline-3-carboxylate, m.p. 164—166° [*carboxylic acid*, m.p. 221—222° (evolution of CO₂)], is obtained by the interaction of (I) and MeI in EtOH-NaOEt. The corresponding 3-Et compound, m.p. 226—228°, is obtained similarly, or by condensing benzanilide imidochloride with CH₂(CO₂Et)₂. Clem-

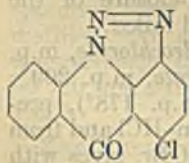
mensen reduction of (I) affords Et 2-phenyl-3:4-dihydroquinoline-3-carboxylate, m.p. 125° (decomp.), but more drastic reduction (EtOH-HCl-Sn; 4—5 hr.; reflux) gives Et 2-phenyltetrahydroquinoline-3-carboxylate (?), m.p. 245°, whilst interaction with PCl₅ affords Et 4-chloro-2-phenylquinoline-3-carboxylate, m.p. 101—103°. Decarboxylation (H₂O; 210—220°; 6 hr.) of 4-hydroxy-2-phenylquinoline-3-carboxylic acid is described. F. N. W.

isoQuinoline series. I. Attempted synthesis of isoquinoline derivatives from substituted benzylamines. B. B. DEY and T. R. GOVINDACHARI. II. **isoQuinolines from opianylmethylamine.** B. B. DEY and T. K. SRINIVASAN (Arch. Pharm., 1937, 275, 383—397, 397—405).—I. CHAc·N·OH with NH₂Ph, NH₂·CH₂Ph, or piperonylamine (I) in C₆H₆ gives β-phenyl-, m.p. 174°, β-benzyl-, m.p. 131°, and β-piperonyl-*iminopropaldoxime*, m.p. 128°, respectively. Reduction of the CH₂O₂-compound could not be effected. CMeAc·N·OH, (I), and a little K₂CO₃ in hot EtOH give Me α-piperonyl-*iminoethyl ketone*, m.p. 105°. (CHO)₂ and (I) give a resin, which did not give an isoquinoline derivative with dehydrating agents. BzCHO and (I) in EtOH give a poor yield of ω-piperonylamino-ω-hydroxyacetophenone, m.p. 121°, which resists ring-closure; AcCHO gives a resin; OH·CHMe·CO₂H and OAc·CHMe·CO₂H give products, from which no basic product is obtained by dehydration. Aq. CH₂O-NaHSO₃ with (I) or 3:4-(OMe)₂C₆H₃·CH₂·NH₂ gives *piperonyl*-, an oil (*hydrochloride*, m.p. 185°), and 3:4-dimethoxybenzyl-aminoacetone nitrile, m.p. 64° (*hydrochloride*, m.p. 188°), respectively; attempted ring-closure of the former product by the Hoesch method failed.

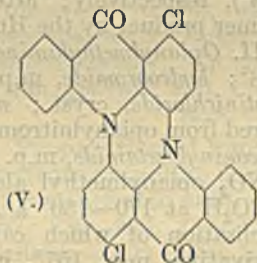
II. **Opianylmethylamine**, an oil (*hydrochloride*, m.p. 248°; *hydrobromide*, m.p. 235°; *picrate*, m.p. 209°; *platinichloride*, *cryst.*; *methiodide*, m.p. 178°), prepared from opianyl nitromethane by Zn-HCl and from meconinylacetamide, m.p. 224°, by NaOBr, gives with HNO₂ opianylmethyl alcohol, m.p. 115°, and with HCO₂H at 170—180° a *HCO* derivative, m.p. 147°, cyclisation of which cannot be effected; the *Ac* derivative, m.p. 157°, however, with P₂O₅ in hot xylene gives the tricyclic *lactone*, an oil (*picrate*, m.p. 242°; *methiodide*, m.p. 207°), of 4-hydroxy-6:7-dimethoxy-1-methyl-3:4-dihydroisoquinoline-5-carboxylic acid, reduced by Zn-HCl to the corresponding *H₄-lactone*, an oil (*picrate*, m.p. 230—232°; *methiodide*, m.p. 242° after sintering from 176°; *Ac* derivative, m.p. 167° after sintering from 100°; with HNO₂ gives an oil); the *Bz* derivative, m.p. 158°, gives similarly the *lactone*, an oil (*picrate*, m.p. 158°), of 4-hydroxy-6:7-dimethoxy-1-phenylisoquinoline-5-carboxylic acid. o-CO₂H·C₆H₄·CHO and MeNO₂ give α-nitromethylphthalide, m.p. 130°, reduced by Zn-HCl to α-amino-methylphthalide, an oil [*hydrochloride*, m.p. 253°; *hydrobromide*, m.p. 245°; *picrate*, m.p. 192°; (?) *methiodide* of the *N-Me₂* derivative, m.p. 240°]; attempts to cyclise the oily *HCO* and *Ac* and *Bz*, m.p. 169—170°, derivatives failed. R. S. C.

Acridine. XVII. Syntheses in the acridone series. K. LEHMSTEDT and K. SCHRADER (Ber., 1937, 70, [B], 1526—1538).—2:6-C₆H₃Cl₂·CO₂H (I), m.p. 139—140° (prep. from 1:2:6-C₆H₃MeCl·NO₂

described), is converted by NH_2Ph , Cu-bronze, and K_2CO_3 in boiling amyl alcohol into diphenylamine-2-carboxylic acid and BzOH . Similar slow change occurs in presence of Na but in absence of catalyst there is no reaction. NPhMe_2 behaves similarly to NH_2Ph . (I) is transformed by conc. $\text{H}_2\text{SO}_4\text{--HNO}_3$ (*d* 1.52) into 2:6-dichloro-3-nitrobenzoic acid, m.p. 152°, which is converted by NH_2Ph at 135–140° into 3-chloro-6-nitrodiphenylamine-2-carboxylic acid (II), m.p. 206°, and 4-nitro-1:3-dianilinobenzene, m.p. 178°, and by boiling NH_2Ph and anhyd. Na_2CO_3 into 3-nitro-2:6-dianilinobenzoic acid, m.p. 167–169° (decomp.). NO_2 cannot be removed from (II) in the usual manner since reduction and diazotisation lead to 6-chloro-1-phenylbenzotriazole-7-carboxylic acid, m.p. 230°. Treatment of (II) with POCl_3 followed by H_2O or by conc. H_2SO_4 at 100° leads to 4-chloro-1-nitroacridone (III), decomp. 249°, nitrated [conc. $\text{H}_2\text{SO}_4\text{--HNO}_3$ (*d* 1.5)— AcOH] to 4-chloro-1:7-dinitroacridone, m.p. 275–277°, which couples with 4-aminodiphenylamine-2-sulphonic acid in PhNO_2 to 1:7-dinitro-4-acridonylaminodiphenylamine-2-sulphonic acid (Na salt), which gives brown-red shades on wool. Cl in (III) is very reactive. Short boiling with NH_2Ph converts (III) into 1-nitro-4-anilinoacridone, m.p. 224°, and treatment of (III) with 1-aminoanthraquinone and K_2CO_3 in PhNO_2 at 206° affords 1-nitro-4-1'-anthraquinonylaminoacridone of very high m.p. Reduction of (III) by $\text{SnCl}_2\text{--conc. HCl}$ gives 4-chloro-1-aminoacridone, m.p. 224–227° (decomp.) when placed in bath preheated to 220°, converted by NaNO_2 and HCl into 4-chloro-1:10-azoacridone (IV), decomp. 218°. 1-Aminoacridone similarly yields



(IV.)



(V.)

1:10-azoacridone, decomp. 258–259°. Both compounds evolve N when heated by themselves or in solvents of high b.p. Under these conditions (IV) gives the compound (V), m.p. 369–371° after darkening when placed in bath preheated to 350°. (IV), 1-aminoanthraquinone, N_3H , NaOAc , and CuCl in boiling tetrahydronaphthalene give the compound, $\text{C}_{54}\text{H}_{28}\text{O}_6\text{N}_4$; the corresponding 5- and 8-NHBz-derivatives are obtained similarly. 1:2:6- $\text{C}_6\text{H}_3\text{MeCl-NO}_2$ is converted into 2-chloro-6-nitrobenzoic acid, the K salt of which is transformed by NH_2Ph , K_2CO_3 , and Cu powder in boiling amyl alcohol into 3-nitrodiphenylamine-2-carboxylic acid, m.p. 172°, from which 4-nitroacridone could not be prepared. K 2-chloro-4-nitrobenzoate, $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{K}$, K_2CO_3 , and Cu powder in boiling amyl alcohol afford 5-nitrodiphenylamine-2:2'-dicarboxylic acid, decomp. 323° after darkening, which is transformed by POCl_3 into 2-nitroacridone-9-carboxylic acid, m.p. 331–333°, decarboxylated by mol. Ag at 290–300°/high vac. to 2-nitroacridone. H. W.

Manufacture of acridine derivatives.—See B., 1937, 842.

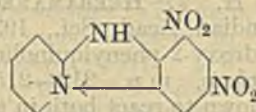
Acridones. XI. Condensation of 5-chloro-2-nitrobenzaldehyde with chloro- and bromobenzene by means of concentrated sulphuric acid. I. TANASESCU and M. MACAROVICI (Bull. Soc. chim., 1937, [v], 4, 240–245).—2:5:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl-CHO}$ (I) with PhCl and H_2SO_4 gives 2:7-dichloro-5-hydroxyacridine 10-oxide (II), m.p. >300° (Na salt; Bz derivative, m.p. 258–260°), hydrolysed by $\text{HCl-EtOH-H}_2\text{O}$ to 2:7-dichloroacridone, m.p. >300°, also obtained from (II) by reduction with $\text{Zn-CaCl}_2\text{-EtOH-H}_2\text{O}$, and converted by $\text{POCl}_3\text{-NPhMe}_2$ into 2:7-dichloro-5-p-dimethylaminophenylacridine, m.p. 240–241°. In addition to (II) a compound, m.p. about 100°, is also obtained. Reduction of (II) with $\text{Na-Hg-NaOH-H}_2\text{O}$ gives 2:7-dichloroacridine 10-oxide, m.p. 220°. Similarly, (I) with PhBr and H_2SO_4 gives 2-chloro-7-bromo-5-hydroxyacridine 10-oxide, m.p. 396° (Bz derivative, m.p. 293°), hydrolysed to 2-chloro-7-bromoacridine 10-oxide, m.p. 290–295°, and converted by $\text{POCl}_3\text{-NPhMe}_2$ into 2-chloro-7-bromo-5-p-dimethylaminophenylacridine, m.p. about 225°. H. G. M.

Preparation of hydantoin from glycine and nitrocarbamide. P. T. SAH and T. F. LIU (Sci. Rep. Nat. Tsing Hua Univ., 1937, 4, A, 31–33).—Details are given for the prep. of hydantoic acid and thence of hydantoin from glycine and $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NO}_2$, each in 90% yield. R. S. C.

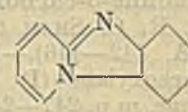
Resistance of diketopiperazinepropionic acid to fission by proteinases. S. AKABORI and S. MAEDA (Proc. Imp. Acad. Tokyo, 1937, 13, 213–216).—The complete resistance of l- and dl-diketopiperazinepropionic acid (prep. from dl-glutamic acid), m.p. 130°, to even large amounts of trypsin and papain is proved by the Sasaki colour reaction (measured in a step-photometer) and by recovery of large amounts of unchanged acid. R. S. C.

Preparation of 1-phenyl-2:3-dimethylpyrazol-5-on-4-yl isopentyl [α -ethylpropyl] ketone.—See B., 1937, 843.

Cyclic 1:3-diazalines. (Sir) G. T. MORGAN and (Miss) J. STEWART (Chem. and Ind., 1937, 670).—2-Aminopyridine and picryl chloride give a picryl derivative, which when heated forms a $(\text{NO}_2)_2$ -compound (I) (?). Reduction and elimination of NH_2 leads to 1:2-pyrido-4:5-benz-1:3-diazaline (II), isomeric with 3-carboline. 2-Amino-3-methylpyridine and 1-aminoisquinoline similarly afford 3'-methyl-1:2-pyrido- and 1:2-isquinolo-7:9-dinitro-4:5-benz-1:3-diazaline.



(I.)

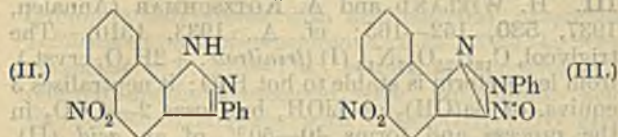


(II.)

F. R. S.

Aromatic nitro-derivatives. XII. Action of certain hydrazines on 1-chloro-2:4-dinitronaphthalene. A. MANGINI (Atti R. Accad. Lincei, 1937, [vi], 25, 326–332).—1:2:4- $\text{C}_{10}\text{H}_5\text{Cl(NO}_2)_2$ (I) with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH at 20° for 3 days gives

4:4'-dinitro-2:2'-azoxynaphthalene, with some 5-nitro-3-hydroxynaphthotriazole (A., 1926, 163). With $\text{NH}_2\text{N}:\text{CHPh}$, (I) gives *benzaldehyde-2:4-dinitro- α -naphthylhydrazine*, m.p. 204—204.5°, converted by NaOH into 5-nitro-3-phenyl- $\beta\alpha$ -naphthopyrazole (II), m.p. 289—290° (decomp.) (*Ac* derivative, m.p. 175—



176.5°). With $\text{NHPh}\cdot\text{NH}_2$, (I) yields directly 5-nitro-2-phenyl- $\beta\alpha$ -naphthotriazole 3-oxide (III), m.p. 182.5—183.5°. $p\text{-NO}_2\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ gives N-2:4-dinitro- α -naphthyl-N'-p-nitrophenylhydrazine, converted by AcOH into 5-nitro-2-p-nitrophenyl- $\beta\alpha$ -naphthotriazole 3-oxide, m.p. 288—289° (decomp.).

E. W. W.

Derivatives of lin.-benzoquinoxaline. H. GOLDSTEIN and M. STREULI (Helv. Chim. Acta, 1937, 20, 650—653).—Condensation of 2:3- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ with the appropriate *o*-diketone affords the following lin.-quinoxalines: 2:3-dimethyl- [2:3-dimethyl-



6':7'-benzoquinoxaline] (I), m.p. 211°, and 2:3-diphenyl-lin.-benzoquinoxaline, m.p. 192°; *phenanthro-lin.-naphthazine* [1':2':3':4':7':8'-tribenzophenazine], m.p. 302°, 2-hydroxy-3-methyl-, m.p. 290° (decomp.), and 2:3-perinaphthylene-lin.-benzoquinoxaline (II), m.p. 360°.

P. G. C.

Compounds of cinnamaldehyde with skatole. V. DOSTÁL (Chem. Listy, 1937, 31, 250—252).—Skatole and cinnamaldehyde in EtOH with H_2SO_4 yield colourless 3:3'-dimethyl-2:2'-di-indolylstyryl-methane, m.p. 73°, converted by oxidation (FeCl_3 in EtOH- H_2SO_4) into blue 3:3'-dimethyl-2:2'-di-indolylstyrylcarbinol (I), m.p. 117°. Evaporation of Et₂O solutions of (I) yields a red substance, $\text{C}_{27}\text{H}_{28}\text{ON}_2$ or $\text{C}_{27}\text{H}_{26}\text{ON}_2$, m.p. 105°, converted into a yellow substance, $\text{C}_{27}\text{H}_{26}\text{N}_2$, m.p. 142—145°, when shaken with aq. alkalis; the red and yellow substances regenerate (I) when treated with aq. acids.

R. T.

Manufacture of polyamino-1:9-anthrapyrimidines.—See B., 1937, 764.

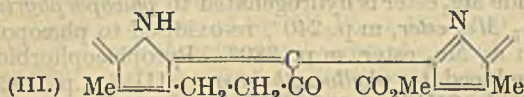
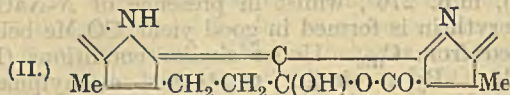
Chlorophyll. LXXVII. Phaeoporphyrinogen a_5 , phylloerythrinogen, and attempted inactivation of chlorophyll and its derivatives. H. FISCHER and K. BUB (Annalen, 1937, 530, 213—230).—Inactivation of chlorophyll can probably be achieved only by synthetic means. Isomerisation processes which are not clearly understood give an appearance of racemisation; achievement of the latter is complicated by the no. of asymmetric centres. Hydrogenation (Pd-sponge in AcOH) of phaeophorbide *a* gives *phaeoporphyrinogen a₅* (I), $\text{C}_{35}\text{H}_{42}\text{O}_5\text{N}_4$, m.p. 242°, $[\alpha] \pm 0^\circ$ in COMe_2 or 20% HCl. Reduction proceeds in the same manner as with HI in that 2 H from

nucleus III wander to the vinyl group of nucleus II. Re-oxidation of (I) gives exclusively *phaeoporphyrin a₅* (II), m.p. 276°, whilst in presence of *N*-NaOH *phylloerythrin* is formed in good yield, CO_2Me being removed from C_{10} . Under similar conditions (II) is stable. By a similar treatment, methylphaeophorbide Me_2 ester is hydrogenated to *phaeoporphyrinogen a₅ Me₂ ester*, m.p. 240°, re-oxidised to *phaeoporphyrin a₅ Me₂ ester*, m.p. 280°. Pyrophaeophorbide *a* is reduced to *phylloerythrinogen* (III), m.p. 202°, $[\alpha] + 0^\circ$ in CHCl_3 or 20% HCl, re-oxidised to *phylloerythrin*; an oxime of (III) could not be obtained. Hydrogenation of mesophaeophorbide *a* in COMe_2 gives an apparently optically inactive product after absorption of 5 H; the leuco-compound could not be obtained cryst. but oxidation of it leads to optically inactive *mesophaeophorbide a* (III), m.p. 218°. It is converted by boiling $\text{C}_5\text{H}_5\text{N}\cdot\text{KOH}\cdot\text{MeOH}$ into *mesochlorin e₆* [*Me* ester (IV), m.p. 184°, $[\alpha] \pm 0^\circ$ in COMe_2], further transformed by prolonged boiling with $\text{C}_5\text{H}_5\text{N}$ into *mesochlorin e₄*, m.p. 195°, $[\alpha]_D \pm 0^\circ$ in COMe_2 . Treatment of (III) with boiling $\text{C}_5\text{H}_5\text{N}$ affords mesopyrophorbide *a*, $[\alpha] - 230^\circ$ in COMe_2 . (IV) is transformed by $\text{C}_5\text{H}_5\text{N}\cdot\text{KOH}\cdot\text{MeOH}$ into "ring-synthetic" mesophaeophorbide *a* $[\alpha] \pm 0^\circ$ in COMe_2 . (III) is converted by $\text{KOH}\cdot\text{PrOH}$ into mesopurpurin 7. The transformations of (III) into mesopurpurin 18, m.p. 262°, $[\alpha] + 222^\circ$ in 20% HCl, mesochlorin *p₆* *Me* ester, $[\alpha]_D + 135^\circ$ in 20% HCl, and meso-*ψ*-chlorin, m.p. 188°, $[\alpha] - 149^\circ$ in COMe_2 , are recorded. Mesochlorin *e₆* *Me₂ ester*, $[\alpha] - 48^\circ$ in COMe_2 , as Na salt is transformed by BzCl in $\text{C}_5\text{H}_5\text{N}$ at 0° into the *anhydride*, $\text{C}_{43}\text{H}_{46}\text{O}_2\text{N}_4$, m.p. 195°, $[\alpha] \pm 0^\circ$ in COMe_2 , which with boiling glycol gives the *glycol ether*, m.p. 168°, $[\alpha] - 180^\circ$ in COMe_2 ; this with anhyd. Na_2CO_3 in boiling $\text{C}_5\text{H}_5\text{N}$ affords mesopyrophaeophorbide *a*, m.p. 232°, $[\alpha] - 350^\circ$ in COMe_2 . Inactive mesophaeophorbide *a* is converted into mesochlorin *e₆* *Me₂ ester*- Bz_2O and thence by $\text{C}_5\text{H}_5\text{N}$ at 100° into mesochlorin *e₆* *Me₂ ester*, m.p. 205°, $[\alpha] - 48^\circ$ in COMe_2 ; this with BzCl gives a compound with $[\alpha] \pm 0^\circ$ in COMe_2 transformed by boiling $\text{C}_5\text{H}_5\text{N}$ into the di-ester with $[\alpha] - 77^\circ$ in COMe_2 . Phaeopurpurin 7 ester (V) is hydrogenated (Pd-sponge in COMe_2) to the leuco-compound, $[\alpha] + 235^\circ$ in COMe_2 , re-oxidised to (V) with $[\alpha] + 201^\circ$ in COMe_2 . Similarly phaeopurpurin 18 (VI) is hydrogenated to a substance, $[\alpha] + 259^\circ$ in COMe_2 , re-oxidised to (VI) with $[\alpha] + 628^\circ$ in COMe_2 . Chlorin *p₆* ester (VII) yields a hydro-compound, $[\alpha] \pm 0^\circ$, from which (VII) is regenerated with $[\alpha] + 129^\circ$ in COMe_2 . *ψ*-Chlorin *p₆* ester (VIII) yields a leuco-compound with $[\alpha] \pm 0^\circ$ in COMe_2 , re-oxidised to (VIII) with $[\alpha] - 133^\circ$ in COMe_2 . Attempts are described to racemise pyrophaeophorbide *a* in PhNO_2 and chlorin-*e₆* in NaOH.

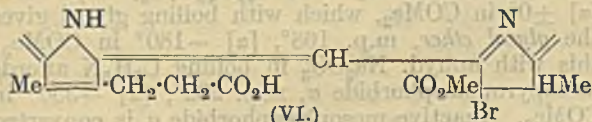
H. W.

Chlorophyll. LXXIX. Anhydrochlorins, rhodorrhodin, and catalytic reduction of porphyrins to chlorins. H. FISCHER and K. HERRLE (Annalen, 1937, 530, 230—256).—Mesorhodochlorin (I) is converted by P_2O_5 at 100° into *rhodorrhodin* (II), m.p. > 330°, which is somewhat unstable and is almost completely decomposed by BzCl in $\text{C}_5\text{H}_5\text{N}$ or HCl-MeOH. It is converted by boiling glacial AcOH into

rhodoporphyrin- γ -carboxylic anhydride and by CH_2N_2 in Et_2O into rhodorhodin Me ester (III), m.p. 298° .



Oxidation of rhodoporphyrin dihydrazide with KMnO_4 affords rhodoporphyrin and (II). Similarly oxidation of rhodoporphyrin monohydrazide Me ester yields (III). Treatment of (I) with oleum at room temp. and of the product with CH_2N_2 gives anhydromesorhodochlorin Me ester, m.p. 279° (salt, $\text{C}_{33}\text{H}_{34}\text{O}_3\text{N}_4\text{Cu}$, m.p. 308° ; anhydromesorhodochlorin, m.p. 257°), attempted oximation of which gives a dye identical with that obtained similarly from (II). Mesopyrrochlorin is transformed by P_2O_5 and sand or, preferably, by oleum into anhydromesopyrrochlorin (IV), m.p. 270° (salt, $\text{C}_{31}\text{H}_{32}\text{ON}_4\text{Cu}$, m.p. 292°), which is degraded to pyrrohodin (V) by HI or by AgOAc and AcOH . (IV) is converted by $\text{NH}_2\text{OH}\cdot\text{HCl}$ in boiling $\text{C}_6\text{H}_5\text{N}$ into the oxime, m.p. 265° . Pyrrochlorin is dehydrated to anhydropyrrrochlorin, $\text{C}_{31}\text{H}_{32}\text{ON}_4$, m.p. 246° , which is degraded by HI to (V), and gives an additive product with $\text{CHN}_2\cdot\text{CO}_2\text{Et}$. Vinylpyrrochlorin Me ester in CHCl_3 is converted by $\text{Fe}(\text{OAc})_2$ and NaCl in AcOH into the corresponding haemin, which with resorcinol at 180° gives 2-de-ethylpyrrochlorin Me ester, m.p. 230° . Meso-



rhodochlorin Me ester is readily brominated in CHCl_3 to the compound (VI), m.p. 165° after softening, the constitution of which follows from its conversion by $\text{KOH}\cdot\text{MeOH}$ into rhodoporphyrin and by AgOAc in AcOH into a dye of the type of the dihydroxychlorins. Pyrrochlorin (VII) is hydrogenated (Raney Ni in dioxan at 60°) to leuco-compounds which could not be caused to crystallise and are re-oxidised by air, thus giving the original material and mesopyrrochlorin, m.p. $240\text{--}250^\circ$, also obtained by hydrogenation in BuOH or NPhMe_2 and converted by $\text{AgOAc}\cdot\text{AcOH}$ into (VII). Similar hydrogenation of phylloporphyrin gives a chlorin which is not spectroscopically identical with mesophyllochlorin and the product derived from porphyrinmonocarboxylic acid 7 differs from the synthetic material. Hydrogenation (Pd) of pyrrochlorin Me ester Zn salt yields a chlorin complex. H. W.

Highly coloured condensation products from benzamidine and glyoxal. I. J. B. EKELEY and A. R. RONZIO (J. Amer. Chem. Soc., 1937, 59, 1313—1316).—The action of NaOEt and EtOH under various conditions on benzamidine-glyoxal (A., 1935, 1133) yields glyoxaline-red, and the compounds, $(\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}_4)_2\text{O}$ (deep purple), m.p. 326° , $\text{C}_{42}\text{H}_{30}\text{O}_6\text{N}_8$ (green), m.p. 264° , and $\text{C}_{22}\text{H}_{20}\text{O}_3\text{N}_4$ (orange), m.p.

249° (structures suggested). The benzamidine-glyoxal mother-liquors yield a compound, $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_4$ (dark red), m.p. 183° , possibly 1:3-dibenzamidyl-4:6-dihydroxyquinol. A. Li.

Wing pigments of common white butterflies.

III. H. WIELAND and A. KOTZSCHMAR (Annalen, 1937, 530, 152—165; cf. A., 1933, 1310).—The triglycol, $\text{C}_{19}\text{H}_{25}\text{O}_{17}\text{N}_{15}$ (I) (trinitrate, $+2\text{H}_2\text{O}$, cryst.), from leucopterin is stable to hot H_2O ; it neutralises 3 equivs. of $\text{Ba}(\text{OH})_2$ or LiOH , but loses 2—4 CO_2 in the process and forms 40—50% of an acid (II), $\text{C}_{14}\text{H}_{18}\text{O}_{13}\text{N}_{10}$, about 15% of a base, $\text{C}_{15}\text{H}_{21}\text{O}_{11}\text{N}_{13}$, cryst. [(? tri)hydrochloride, m.p. $227\text{--}230^\circ$ (decomp.), loses HCl when kept], and 0.1 mol. of $\text{H}_2\text{C}_2\text{O}_4$ [not a by-product of the formation of (II), but possibly of the base]. (II) titrates as a tribasic acid, but gives a hydrochloride, gives no murexide test, and does not reduce ammoniacal AgNO_3 ; it is stable to $\text{Pb}(\text{OAc})_4$, as also is uric acid glycol; with $\text{Ba}(\text{OH})_2$ at 90° it gives 6 mols. of NH_3 , 3 of CO_2 , and 3 of $\text{H}_2\text{C}_2\text{O}_4$; with dil. HCl at $30\text{--}40^\circ$ it gives a little NH_4Cl and $\text{H}_2\text{C}_2\text{O}_4$ and a monobasic acid, $\text{C}_{13}\text{H}_{18}\text{O}_{11}\text{N}_{10}$, decomp. $260\text{--}270^\circ$; with 25% HCl at 70° it gives 2 mols. of $\text{H}_2\text{C}_2\text{O}_4$, 1 mol. of NH_3 , and 50% of a base, (?) $\text{C}_8\text{H}_{14}\text{O}_2\text{N}_{10}\cdot\text{H}_2\text{O}$ or $\text{C}_4\text{H}_7\text{ON}_5\cdot 0.5\text{H}_2\text{O}$ (hydrochloride, decomp. about 200° with red coloration; cf. ψ -uric acid), which gives no murexide test and does not reduce $\text{AgNO}_3\cdot\text{NH}_3$, but gives a red Ag salt. The by-product, m.p. $>370^\circ$ (decomp.), obtained in the prep. of (I) is a weak base, $\text{C}_{11}\text{H}_{20}\text{O}_{11}\text{N}_{10}$, stable to hot H_2O , giving no CO_2 with HCl , and liberating NH_3 and a little CO_2 with alkali. This base is also formed along with much (I) by the action of 0.2N-HCl on anhydro-leucopterin, the relations of which to leucopterin are discussed. The H_2O -sol. dye of the wings is fractionated by $(\text{NH}_4)_2\text{SO}_4$ into a blue and a green component; the mixture readily liberates its albumin, which gives Gmelin's reaction for gallic dyes; the dye resembles oocyanin in many respects and is probably of the same type. The Et_2O -extract of the wings yields, after hydrolysis by KOH , cholesterol, palmitic, oleic, and linolenic acid. R. S. C.

Manufacture of amide derivatives of isooxaz-olecarboxylic acids.—See B., 1937, 843.

Preparation of 1-methylbenzoxazole. B. BEIL-ENSON (J.S.C.I., 1937, 56, 302T).— $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ and Ac_2O in aq. suspension give $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, converted by P_2O_5 (75% yield) into 1-methylbenzoxazole.

Condensation of aromatic aldioximes with esters of β -ketonic acids. R. FUSCO and C. MUSANTE (Gazzetta, 1937, 67, 248—256).—The products from $\text{CHR}\cdot\text{N}\cdot\text{OH}$ ($\text{R} = \text{Ph}$ or $p\text{-OMe}\cdot\text{C}_6\text{H}_4$), regarded by Minunni and D'Urso as α -benzylidene- (A., 1928, 1245) and α -anisylidene-aminocrotono- β -lactone (A., 1929, 555), are actually 4-benzylidene- and 4-anisylidene-3-methyl-5-isooxazolone. Similarly " α -benzylidene-" (A., 1928, 1245) and " α -anisylidene-aminocinnamo- β -lactone" (A., 1929, 555) are 3-phenyl-4-benzylidene- and -4-anisylidene-5-isooxazolone (I), also prepared from $\text{CHR}\cdot\text{N}\cdot\text{OH}$ and $\text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{Et}$. The product from (I) and NH_2OH is not aminocinnamo- β -lactone (A., 1929, 556), but

3-phenyl-5-isooxazolone. Araldoximes when heated with ZnCl_2 are partly isomerised to amides.

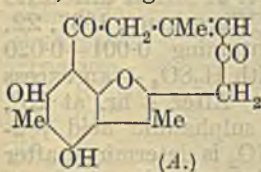
E. W. W.

Quinoline derivatives. II. T. N. GHOSH (J. Indian Chem. Soc., 1937, 14, 123—126; cf. this vol., 309).—Attempts have been made to prepare new quinoline derivatives with anti-malarial properties. 1-Phenyl-3-methylpyrazolino-4:5-(2':3')-4'-hydroxyquinoline, m.p. 175—176°, results by condensing 1-phenyl-3-methylpyrazolone with anthranilic acid. Et α -urethanylacetate with $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$ gives Et α -urethano- o -nitrocinnamate, m.p. 227—228°, reduced to o -aminocinnamic acid and not 2-hydroxy-3-urethanoquinoline. Condensation of hippuric acid with anthranilic acid gives 1-keto-3-benzamido-methyl-5:6-benz-2:4-oxazine, m.p. 205—207° (o -nitrobenzylidene derivative, m.p. 234—235°).

D. J. B.

Lichen substances. LXXXII. Usnic acid. III. Y. ASAHINA and M. YANAGITA [with S. KAWAMURA] (Ber., 1937, 70, [B], 1500—1505).—At room temp. usnic acid (I) has 2 active H (Zerevitinov) whilst at higher temp. 3 active H are present; decarboxylic acid (II) has 3 active H. The oxime anhydride of (II) is oxidised by H_2O_2 to the dicarboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}\equiv\text{C}\cdot\text{O}\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, decomp. 202°

after softening at 180°, thus giving further evidence of the 1:3-diketone side-chain attached to the furan nucleus. The isodecarboxylic acid, m.p. 197°, of Widman is also obtained by the action of EtOH or (II) at 170°; it is not an isomeride of (II) but is decacetylcarboxylic acid, $\text{C}_{15}\text{H}_{16}\text{O}_5$ (dihydrazone, decomp. 196—197°). (I) is transformed by conc. H_2SO_4 at 50—60° into usnic acid (III), m.p. 230—231° (decomp.) after softening at about 210°; this is a true carboxylic acid since it is converted by HCl-EtOH into an ester and by warm NH_2Ph into decarboxusanilide, m.p. 235—236°. Similar treatment of (II) with conc. H_2SO_4 yields decarboxanol (IV), $\text{C}_{17}\text{H}_{16}\text{O}_5$, m.p. 209°, which gives a very pronounced Ehrlich reaction;



it is also formed from (III) and Cu-bronze. (IV) is unimol. and therefore an internal condensation product of (II). Since loss of H_2O cannot occur from the 1:3-diketone side chain it follows that Ac

of the phloroglucinol nucleus must be involved so that (V) is very probably A.

H. W.

β -Naphthothiazine (thio- β -naphthylamine) and its derivatives. H. Y. FANG, C. L. LIU, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1937, 4, A, 21—26).— $\text{NH}(\text{C}_{10}\text{H}_7\text{-}\beta)_2$ and S (2 atoms) at 190° give β -naphthothiazine, 2:3- $\text{C}_{10}\text{H}_7\text{-}\langle\text{NH}\rangle\text{S}\text{-}\text{C}_{10}\text{H}_7\text{-}$ 2:3, m.p. 222—223° [dipicrate, m.p. 250—251° (decomp.); styphnate, m.p. 262—263° (decomp.)].

R. S. C.

Anthrylthiocarbimides, anthrathiazoles, and thiolanthrathiazoles. M. BATTEGAY and P. BOEHLER (Compt. rend., 1937, 204, 1477—1479).—The aromatic nature of α - (I) and β - (II) -anthramine is illustrated further. CS_2 almost quantitatively con-

verts (I) in $\text{C}_5\text{H}_5\text{N}$ into di-1-anthrylthiocarbamide (III), m.p. 234°, giving with warm Ac_2O 1-anthrylthiocarbimide, m.p. 99°, from which (III) is regenerated by the action of (I) in PhMe. Similarly (II) gives di-2-anthrylthiocarbamide, m.p. 262°, and 2-anthrylthiocarbimide, m.p. 196°. S, (I), and HCO-NH_2 at 200° give 1':2'-anthra-4:5-thiazole, m.p. 132°, the constitution of which is established by its oxidation by HNO_3 to an anthraquinone derivative containing S. 1':2'-Anthra-5:4-thiazole, m.p. 166°, is obtained from (II). Di-2-aminodianthryl disulphide is converted into 2-thiol-1':2'-anthra-5:4-thiazole, m.p. 300°.

H. W.

Manufacture of dyes [thiazole derivatives etc.].—See B., 1937, 764.

Indigoid vat dyes of the isatin series. II. 3-Indole-1'-(5'-methyl)thionaphthenindigos. S. K. GUHA (J. Indian Chem. Soc., 1937, 14, 240—244; cf. A., 1934, 1013).—The 5-Cl-, 5-Br-, 5:7-Br₂-, 5-bromo-7-nitro-, and 5:7-(NO_2)₂-derivatives of 3-indole-1'-(5'-methyl)thionaphthenindigo are prepared from isatin or a derivative and the appropriate 3-hydroxythionaphthen derivative in AcOH in presence of HCl. They dye wool (acid bath) and cotton (vat) in red shades lighter than those given by the corresponding 5'-Me derivatives, in conformity with Martinet's rule.

P. G. C.

Alkaloid from the Equisetaceæ family. E. GLET and J. GUTSCHMIDT (Apoth.-Ztg., 1937, 52, 265—266).—*Equisetum palustre* contains a hydrocarbon, $\text{C}_{21}\text{H}_{42}$, m.p. 77°, and a mixture of alkaloids, mainly palustrine, $\text{C}_{12}\text{H}_{24}\text{O}_2\text{N}_2$, b.p. 205—210°/0.1 mm. (hydrochloride, m.p. 181°, $[\alpha]_D$ 0).

R. S. C.

Microscopical examination of ergot alkaloids. II. Ergotinine, ergotoxine, and sensibamine. A. KOFLER (Arch. Pharm., 1937, 275, 455—467; cf. A., 1936, 1527).—The crystallo-optical properties (photomicrographs) of ergotinine (3 forms), m.p. 220° (decomp. from 210—215°), ergotoxinine, m.p. 165° (decomp. from 100°), and sensibamine, m.p. 180—182°, are detailed.

R. S. C.

Presence in the bark of *Corynanthe paniculata*, Welwitsch, of a levorotatory isomeride of yohimbine. RAYMOND-HAMET (Bull. Sci. Pharmacol., 1937, 44, 54—59).—Paniculatine, $\text{C}_{21}\text{H}_{20}\text{O}_3\text{N}_2 + 1.5\text{H}_2\text{O}$ (I), $[\alpha]_D$ -42° in EtOH, hygroscopic, an isomeride of yohimbine (II), is isolated with it from the bark of *C. paniculata*, separation being effected by fractional crystallisation of the more sol. hydrochloride, $[\alpha]_D +45.95^\circ$ in H_2O , of (I). The colour tests of (II) are also given by (I); the latter is more sol. in MeOH at 50°.

R. F. P.

Cotarnine series. IX. Attempts to synthesise alkaloids of the cryptopine types. B. B. DEY and (MISS) P. L. KANTAM (J. Indian Chem. Soc., 1937, 14, 144—150).— o -Toluoylcotarnine, m.p. 99—100° (oxime, m.p. 170°; semicarbazone, m.p. 200°; hydrazone, m.p. 211°), and its $p\text{-NO}_2$ -derivative, m.p. 124—125° (semicarbazone, m.p. 219—220°; oxime, m.p. 175°; hydrazone, m.p. 215°), prepared by benzylation could not be cyclised to compounds containing two isoquinoline rings. Interaction of homophthalonitrile with Ac_2O was likewise un-

successful. 5-Nitrophthalide and cotarnine in Ac_2O give *anhydroacetylcotarnino-5-nitrophthalide*, m.p. 165° . *Anhydrocotarnino-methyl anthranilate*, m.p. 136° , was made by condensing Me anthranilate with cotarnine.

D. J. B.

Isomerism of norcoralydine. E. SPÄTH and W. GRUBER (Ber., 1937, 70, [B], 1538—1540).—Norcoralydine, isolated from the hydrochloride obtained by the condensation of tetrahydropapaverine with 40% CH_2O and 2*N*-HCl at 100° , exists in two forms, (I), m.p. $151.5\text{--}152^\circ$ (vac.), and (II), m.p. $160\text{--}161^\circ$ (vac.). Apparently the base is dimorphous since either (I) or (II) can be caused to separate at will from solutions of either form if a seed is available. The difference is not due to the presence of solvent of crystallisation and there appears no reason to assume a new type of stereoisomerism.

H. W.

Alkaloids of *Veratrum album*. I. Preparation of the alkaloids and their distribution amongst rhizomes, roots, and leaf base. Germ-erine, a new alkaloid of *V. album*. W. POETHKE (Arch. Pharm., 1937, 375, 357—379).—Complex, new methods of extracting and separating the alkaloids of *V. album* are detailed. The crude alkaloids (50) from the rhizomes from Yugoslavia contained *germerine* (I), $\text{C}_{36}\text{H}_{57}\text{O}_{11}\text{N}_2\text{H}_2\text{O}$, m.p. $193\text{--}195^\circ$ (corr.) (7), *protoveratridine* (II) (0.7), *jervine* (III) (0.25), *rubijervine* (IV) (0.2), and amorphous alkaloids (25 g.). Material collected in summer in the Bavarian Alps contained in the roots *protoveratrine* (V) >0.8 , (III) 0.2, (IV), and (I), in the rhizomes (V) 1.33, (I) 1.25, (IV) 0.04, (III) 0.94, and ψ -*jervine* 0.6, and in the leaf base (IV) 0.54, (I) >0.8 , and (III) 0.03 g. per kg. Treatment with $\text{Ba}(\text{OH})_2$ converts (I) into (II), but simultaneously destroys all the (V) present. The constituents vary according to the origin of the plant.

R. S. C.

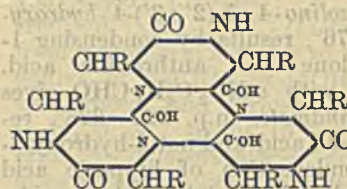
Alkaloids of *Salsola Richteri*. III. Optically active salsoline, and the isolation of two new alkaloids. N. PROSKURNINA and A. OREKHOV (Bull. Soc. chim., 1937, [v], 4, 1265—1274; cf. A., 1934, 907).— $\text{C}_2\text{H}_4\text{Cl}_2$ extracts salsoline (cf. A., 1933, 727), *salsolidine*, m.p. $71\text{--}73^\circ$ (*hydrochloride*, m.p. $233\text{--}235^\circ$; *dihydrate*, m.p. $60\text{--}62^\circ$; *picrate*, m.p. $194\text{--}195^\circ$; *picrolonate*, m.p. $220\text{--}221^\circ$; Bz derivative, m.p. $124\text{--}125^\circ$), and *salsamine*, m.p. $155\text{--}157^\circ$ (decomp.) [*hydrochloride*, m.p. $255\text{--}260^\circ$ (decomp.)]; *picrate*, m.p. $213\text{--}214^\circ$; *picrolonate*, m.p. $220\text{--}221^\circ$], from the leaves and young shoots. Salsoline, a mixture of the *d*- and *dl*-forms, affords a *d*-tartrate from which, after repeated crystallisation, *d-salsoline d-tartrate*, m.p. $215\text{--}216^\circ$ [*d-base*, m.p. $215\text{--}216^\circ$ (*hydrochloride*, m.p. $171\text{--}172^\circ$, $[\alpha]_D +40.1^\circ$ in H_2O)], is isolated. The mother-liquors afford *l-salsoline*, m.p. $214\text{--}215^\circ$ (*hydrochloride*, $[\alpha]_D -39.2^\circ$ in H_2O ; *picrate*, m.p. $214\text{--}215^\circ$; *picrolonate*, m.p. $238\text{--}240^\circ$), which with CH_2N_2 gives *salsolidine*. Equimol. parts of the *d*- and *l*-forms gives a product identical with naturally occurring salsoline.

J. L. D.

New salt of emetine. E. CASERIO (Boll. Chim. farm., 1937, 76, 365—368).—The *dicamphorsulphonate* is described.

F. O. H.

Pattern of proteins. D. M. WRINCH (Proc. Roy. Soc., 1937, A, 160, 59—86; cf. A., 1936, 1528, 1535).—A geometrical theory of the structure of proteins, based on the assumed existence of double and triple peptide linkings, suggests that the mol. is a ring structure produced by the "cyclisation" of polypeptides. Complex mols. are built up from "cyclol



6" mols. (see annexed formula); the resulting laminar mol. has a "front" surface from which side-chains emerge and a "back" surface free from side-chains,

explaining the stability on a H_2O -air interface of proteins one residue thick. The hypothesis allows the construction of laminar mols. with the right order of density, i.e., residue wt. per sq. cm., and explains why chemically different proteins share many properties in common.

G. D. P.

Casein. E. CHERBULIEZ and J. JEANNERAT (Arch. Sci. phys. nat., 1937, [v], 19, Suppl., 51—52).—Casein has three distinct components (α_1 , γ , and δ); α_2 (cf. A., 1933, 843) is $\alpha_1 + \gamma$. Paracasein is $\alpha_1 + \gamma$. Thus Hammarsten's proteose is present in milk.

J. L. D.

Apparatus for centigram elementary analysis.—See A., I, 480.

V.p. of saturated gaseous hydrocarbons.—See A., I, 453.

Modification of the method of Nicloux for the micro-determination of ethyl alcohol. A. IONESCO-MATIU and C. POPESCU (Bull. Soc. Chim. biol., 1937, 19, 911—914).—The titration with aq. $\text{K}_2\text{Cr}_2\text{O}_7$ is used, with leuco-methylene-blue as external indicator. Satisfactory results are obtained with 0.025—0.5% of EtOH.

A. L.

Colorimetric determination of small amounts of carbamide. W. BRANDT (Mikrochem., 1937, 22, 181—186).—The solution [containing 0.001—0.020 mg. of $\text{CO}(\text{NH}_2)_2$] is treated with H_2SO_4 + an excess of 0.02% standard aq. KNO_2 . After 4 hr. at 25° , NaOAc is added, and then sulphanilic acid + α - $\text{C}_{10}\text{H}_7\text{NH}_2$. The excess of KNO_2 is determined after 24 hr. from the intensity of the red coloration produced. Albumin, creatine, uric acid, and glycine do not interfere with the applicability of the method.

J. S. A.

Determination of arginine.—See A., III, 334.

Micro-determination of creatine and creatinine.—See A., III, 344.

Analysis of mixtures of furfuraldehyde and methylfurfuraldehyde. (Miss) E. E. HUGHES and S. F. ACREE (Ind. Eng. Chem. [Anal.], 1937, 9, 318—321).—Use is made of the difference in rates of inter-action of furfuraldehyde and methylfurfuraldehyde with Br in *N*-HCl at 0° to determine the composition of a mixture, the second mol. of Br reacting more rapidly with the Me derivative. The mean error is 0.5 mg. on 3—50 mg.

F. N. W.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

OCTOBER, 1937.

Crystal behaviour of hydrocarbons.—See A., I, 448.

Mechanism of polymerisation. I. Dimeric tetramethylethylene. H. BRUNNER and E. H. FARMER (J.C.S., 1937, 1039—1046).— $\text{CMe}_2\cdot\text{CMe}_2$ polymerised with BF_3 at -10° affords a mixture of dimeric products. With O_3 in light petroleum, the fraction of b.p. $54.9\text{--}56.5^\circ/12$ mm. yields an acid (I), probably *dl*-methylisopropylacetic acid (*amide*, m.p. $121\text{--}122^\circ$); the fraction of b.p. $71\text{--}82^\circ/11.5$ mm. gives CH_2O , a ketone, $\text{C}_9\text{H}_{18}\text{O}_2$ (2 : 4-dinitrophenylhydrazone, m.p. $114\text{--}115^\circ$), and (I). Similarly, the fraction of b.p. $54.9\text{--}58.5^\circ/10.5$ mm. on ozonolysis yielded pinacolone and $\text{CHMePr}^a\cdot\text{CHO}$. Six of the eight theoretically possible hexaldehydes are synthesised by improved methods, and the m.p. of their 2 : 4-dinitrophenylhydrazones, semicarbazones, and dimedon derivatives are recorded below in that order (— signifying no variation from the literature): *iso*-butyl- (99°), $126.5\text{--}127.5^\circ$, 133° , *sec*-butyl- ($93.5\text{--}94.5^\circ$, —, 144°), diethyl- ($94.5\text{--}95^\circ$, $97.5\text{--}99.5^\circ$, $102\text{--}102.5^\circ$), dimethylethyl- (145° , —, $118\text{--}120^\circ$)-acetaldehyde. COMePr^a with Na and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ yields β -methyl- β -*isopropylglycidoacrylate*, hydrolysed ($\text{NaOEt}\cdot\text{H}_2\text{O}$) to *dl*-methylisopropylacetaldehyde, b.p. $115\text{--}117^\circ/770$ mm. (2 : 4-dinitrophenylhydrazone, m.p. $121\text{--}123.5^\circ$; semicarbazone, m.p. $110\text{--}111^\circ$; dimedon derivative, m.p. 162°). J. D. R.

Formation of diene hydrocarbons. I. Principles relating to the course of reaction in the dehydration of unsaturated alcohols. The co-formation of $\alpha\alpha$ - and $\alpha\gamma$ -dimethylbutadiene. R. G. R. BACON and E. H. FARMER (J.C.S., 1937, 1065—1077).— δ -Methyl- Δ^a -penten- δ -ol dehydrated with Br or I yields β -methyl- Δ^a -pentadiene, b.p. $57\text{--}58^\circ/766$ mm., and $\alpha\gamma$ -dimethylbutadiene (I). Similarly, ε -methyl- Δ^b -hexen- δ -ol gives hydrocarbons of b.p. $99\text{--}112^\circ$, which with maleic anhydride afford 3-isopropyl- Δ^4 -tetrahydrophthalic anhydride, m.p. 90° , and on oxidation (KMnO_4) give $\text{Bu}^b\text{CO}_2\text{H}$ and COMe_2 , whilst δ -methyl- Δ^b -penten- δ -ol affords (I) (about 95%) and $\alpha\alpha$ -dimethylbutadiene (about 5%), both of which are dehydration products of β -methylpentane- β -diol. β -Methyl- Δ^b -penten- δ -ol (from β -methylcrotonaldehyde and MgMeI), b.p. $137\text{--}138^\circ$, is dehydrated by HBr to a hydrocarbon, probably containing (I), oxidised to COMe_2 , $\text{H}_2\text{C}_2\text{O}_4$, HCO_2H , and AcOH whilst δ -methyl- Δ^a -penten- γ -ol (improved prep.) is unaffected by HBr or I, but is dehydrated by PhNCO to unidentified conjugated and non-conjugated hydrocarbons. J. D. R.

Synthesis of higher polyenes. R. KUHN (Angew. Chem., 1937, 50, 703—708).—The synthesis of the

following substances is described in historical outline: $\text{Ph}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{Ph}$ ($n=1\text{--}8$), $\text{CO}_2\text{H}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{CO}_2\text{H}$ ($n=1\text{--}5, 7$), $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{CO}_2\text{H}$ ($n=1\text{--}4$), $\text{Me}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{Me}$ ($n=1\text{--}4, 6$), $\text{Me}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{CHO}$ ($n=1\text{--}5, 7$), $\text{Me}\cdot[\text{CH}\cdot\text{CH}]_n\cdot\text{CO}_2\text{H}$ ($n=1\text{--}6, 8$). ζ -Phenylpentadecaheptaenal is converted into the corresponding thioaldehyde and thence into the greenish-black hydrocarbon, $\text{Ph}\cdot[\text{CH}\cdot\text{CH}]_{15}\cdot\text{Ph}$. H. W.

Recent acetylene chemistry. H. VOGL (Österr. Chem.-Ztg., 1937, 40, 373—377).—A review.

Solubility of halogenated hydrocarbon refrigerants in organic solvents. G. F. ZELLHOEFER (Ind. Eng. Chem., 1937, 29, 548—551).—The solubility of CCl_2F_2 , EtCl , CH_2Cl_2 , $\text{C}_2\text{Cl}_2\text{F}_4$, and CFCl_3 in a few, and of MeCl and CHFCl_2 in a large no. of, org. solvents at 32° , under the pressure exerted by the solute at 4.5° , has been determined and the results are discussed. Among the solvents used, the following are new: triethylene glycol Me_2 ether, b.p. 216° ; tetraethylene glycol Me_2 ether, b.p. $115\text{--}118^\circ/2$ mm., and Et_2 ether, b.p. $132\text{--}134^\circ/12$ mm.; tetrahydrofurfuryl ether of $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{OBu}$, b.p. 246° ; diethylene glycol ditetrahydrofurfuryl ether, $199\text{--}203^\circ/14$ mm.; hexaethylene glycol Me_2 ether, b.p. $195\text{--}199^\circ/14$ mm.; 2 : 3-di- β -ethoxyethoxydioxan, b.p. $161\text{--}166^\circ/2$ mm.; 2 : 3-di- β -methoxy- β -ethoxyethoxydioxan, b.p. $210\text{--}220^\circ/2$ mm.; Bu carbitol chloride, b.p. 215° ; ethylene glycol ($\text{C}_2\text{H}_4\text{Cl}$) $_2$ ether, b.p. $80\text{--}85^\circ/2$ mm.; triethylene glycol chloride Me ether, b.p. $116\text{--}117^\circ/12$ mm.; carbitol methoxyacetate, b.p. $128\text{--}132^\circ/7$ mm., ethoxyacetate, b.p. $155\text{--}160^\circ/15$ mm., and laevulate, b.p. $175\text{--}182^\circ/14$ mm.; diethylene glycol dimethoxyacetate, b.p. $204\text{--}208^\circ/17$ mm., and diethoxyacetate, b.p. $210\text{--}215^\circ/15$ mm.; Me carbitol acetate, b.p. $79^\circ/10$ mm., and methoxyacetate, b.p. $145\text{--}149^\circ/15$ mm.; triethylene glycol dimethoxyacetate, b.p. $230\text{--}234^\circ/15$ mm., and methoxyacetate, b.p. 244° ; trimethylene glycol dimethoxyacetate, b.p. $180\text{--}184^\circ/20$ mm.; tetrahydrofurfuryl methoxyacetate, b.p. $136\text{--}140^\circ/18$ mm.; ethylene glycol diethoxyacetate, b.p. $163\text{--}165^\circ/14$ mm.; ethylene glycol Bu $_1$ ether methoxyacetate, b.p. $136\text{--}140^\circ/18$ mm., *n*-butyrate, b.p. 220° , acetate, b.p. 192° , and laurate, b.p. $188^\circ/8$ mm.; triethylene glycol acetate Me ether, b.p. 253° ; ethylene glycol Et $_1$ ether succinate, b.p. $159\text{--}162^\circ/5$ mm.; ethylene glycol CH_2Ph ether acetate, b.p. $122\text{--}125^\circ/5$ mm.; ethylene glycol tetrahydrofurfuryl ether acetate, b.p. $112^\circ/6$ mm.; glycerol- $\alpha\gamma$ -dichlorohydrin adipate, b.p. $235\text{--}240^\circ/8$ mm.; di- β -chloroethyl phthalate, b.p. $198^\circ/5$ mm.; Bu $_2$ dichlorophthalate, b.p. $200\text{--}210^\circ/7$ mm.; benzenesulphonyl-*n*-butylaniline, b.p. $190\text{--}200^\circ/6$ mm. R. C. M.

Determination of tetranitromethane. C. K. KRAUZ and J. M. ŠTEPÁNEK (Chem. Obzor, 1937, 12, 81—85).—In neutral aq. solution 1 mol. of $C(NO_2)_4$ reacts with 2KI exactly, and the I is titrated with standard $Na_2S_2O_3$. About 5 hr. are required for a determination. In an acid medium secondary reactions cause a higher separation of I, so that 1 mol. of $C(NO_2)_4 \rightarrow 2KI + k$, where k increases linearly with the acidity of the solution titrated. The acidity must be determined by a separate titration. In presence of $NaHCO_3$, owing to secondary reactions the separation of I never reaches the theoretical and results of titrations must be corr. from a graph constructed from empirical results. The time of reaction in a neutral medium may be reduced to 10—15 min. with an accuracy of determination of $\pm 0.2\%$ by using EtOH solutions, where, owing to partial oxidation of EtOH by $C(NO_2)_4$, a correction must be applied.

F. R.

Catalytic dehydrogenation of a tertiary alcohol to a ketone. L. MARTINEAU and C. PRÉVOST (Compt. rend., 1937, 205, 154—156).— Bu^tOH , freed from ketonic substances, is dehydrogenated by $Cu-ThO_2$ at 130° to CMe_2CH_2 and a small amount of $COMeEt$. A theoretical explanation of the reaction is suggested.

J. L. D.

Ethoxides and isopropoxides of manganese and rhenium. J. G. DRUCE (J.C.S., 1937, 1407—1408).—Addition of $MnCO_3$ or $Re_2(CO_3)_2$ to HCl or HBr in EtOH or Pr^iOH yields the following compounds: $MnCl_2.EtOH$; $MnCl_3.Pr^iOH$; $MnBr_2.EtOH$; $MnBr_3.Pr^iOH$; $ReCl_3.EtOH$; $ReCl_3.Pr^iOH$. Treatment of the appropriate halide-alcoholate with $NaOEt$ or $NaOPr^i$ affords $Mn(OEt)_2$, *Mn isopropoxide*, *Re triethoxide* and *triisopropoxide*.

J. D. R.

Stereochemistry of deuterium compounds of the type $RR'CX_nX_n$: ethyl- d_4 -ethylcarbinol. F. C. MCGREW and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 1497—1500).—Na and a little Fe [prepared by addition of Na to hydrated $Fe(NO_3)_3$] in liquid NH_3 , treated at -50° to -60° first with C_2H_2 and then with $EtCHO$, give Δ^a -pentinen- γ -ol, b.p. $121-124^\circ/750$ mm. (3:5-dinitrobenzoate, m.p. 91°); the *H phthalate*, m.p. 72° , thereof is partly resolved by brucine to yield an impure 1- Δ^a -pentinen- γ -ol, $[\alpha]_D^{25} -15.25^\circ$. This with H_2-PtO_2 in $EtOAc$ gives CH_3Et_2OH , $[\alpha]_D 0 \pm 0.01^\circ$ [3:5-dinitrobenzoate (II), m.p. $99-99.5^\circ$]. D_2-PtO_2 gives $\alpha\alpha\beta\beta$ -tetra-deutero-*n*-pentan- γ -ol, $[\alpha]_D 0 \pm 0.01^\circ$ [3:5-dinitrobenzoate, m.p. $98.5-99^\circ$, not depressed by admixture with (II)]. This makes it improbable that compounds $CRR'R''R'''$, in which R and R' are alkyl and R is substituted by D, will show measurable $[\alpha]$. Calculation by Boys' method, admittedly untrustworthy, gives an expected $[\alpha]$ 0.01° for $C_6D_5-CHPh-NH_2$; the val. of Clemons *et al.* (-5.7°) may be erroneous.

R. S. C.

Free radicals in organic decomposition reactions. I. Thermal decomposition of mixtures of methyl ether and deutoacetone. E. W. R. STEACIE and W. A. ALEXANDER (Canad. J. Res., 1937, 15, B, 295—304).—The H_2 produced by heating an equimol. mixture of Me_2O and $CO(CD_3)_2$ at 590° for 5 min. contains the same amount (3%) of D_2 as that obtained by decomp. Me_2O and $CO(CD_3)_2$

separately, mixing the products, and heating at 590° for 5 min., indicating that no at. H is produced during the decomp. of Me_2O or of its primary decomp. product, CH_3O . The D_2 is determined by freezing out all but CO and H_2 , burning these, and distilling and analysing the H_2O .

A. LI.

Drying of ether. N. SCHOORL (Pharm. Weekblad, 1937, 74, 1108—1109).—"Wet" Et_2O when dried with Na_2SO_4 or $CaSO_4 \cdot 0.5H_2O$ contains about 0.6% of H_2O (test: turbidity with 2 vols. of CCl_4) and $<0.35\%$ when dried with $MgSO_4$ (test: no turbidity with 2 vols. of CS_2).

S. C.

Molecular structure of $\beta\gamma$ -epoxybutanes.—See A., I, 448.

Mono- and di-hydroxymethylene dimethyl ether. J. LÖBERING and A. FLEISCHMANN (Ber., 1937, 70, [B], 1680—1683).— $CH_2(OMe)_2$ obtained from $MeOH$, $(CH_2O)_n$, and HCl at 100° is contaminated with about 33% of $MeOH$, from which it can be freed by $p-NO_2-C_6H_4COCl$ but not by distillation. It can be obtained pure by repeated passage of CH_2Cl_2 over $NaOMe$ on pumice at 200° or by heating $NaOMe$ and $CH_2Cl \cdot OMe$ (1:1 mol.). $(OMe \cdot CH_2)_2O$ is best obtained by gradual addition of $(CH_2Cl)_2O$ to $NaOMe$ free from $MeOH$.

H. W.

Sulphonic and sulphuric esters as alkylating agents in liquid ammonia. A. L. KRANZFELDER and F. J. SOWA [with (in part) K. J. SCHUEPPERT] (J. Amer. Chem. Soc., 1937, 59, 1490—1492).—Slow addition of $p-C_6H_4Me \cdot SO_3R$ ($R = Me, Pr^i$, or Bu^i), sometimes in Et_2O , to the Na derivatives of $PhOH$, C_6H_5 , $CuOH$, or $C_5H_{11}OH$ in liquid NH_3 gives 37—47% of the appropriate ether or acetylene; $Pr^i_2SO_4$, $Pr^i_2SO_4$, and $(n-C_5H_{11})_2SO_4$ give 29—50% yields; $NaPhSO_4$ gives 60—88% yields of Ph alkyl ethers, but only 25% of Ph_2O . Best yields are obtained by using 2 mols. of ester. Cryst. esters insol. in liquid NH_3 (e.g., $p-C_6H_4Me \cdot SO_3C_5H_{11}$ and $p-C_6H_4Me \cdot SO_3Ph$) do not react, neither does $NaOPh$ or $NaHC_2$ with $n-C_5H_{11} \cdot OAc$, or Bu_3PO_4 with Bu^iOH . γ -Methyl- Δ^a -butinene is prepared, but not described. Prep. of $p-C_6H_4Me \cdot SO_3Bu^i$, b.p. $170-172^\circ/10$ mm. (98% yield), $Pr^i_2SO_4$, b.p. $120^\circ/20$ mm. (quant. yield from cyclopropane and H_2SO_4), and $Pr^i_2SO_4$ (50% yield from $CHMe \cdot CH_2$ and H_2SO_4) is described.

R. S. C.

Tribromoethyl borate. A. MANGINI (Riv. Biol., 1937, 22, 457—462).— $CBBr_3 \cdot CH_2OH$ (I) (avertin) with BBr_3 in light petroleum yields tribromoethyl borate (II), m.p. $179-182^\circ$, sol. in fats and readily hydrolysed by H_2O . (II) resembles (I) in narcotic properties. The lack of narcotic action in other derivatives of (I) is due to non-liberation of the alcoholic OH of (I) in the organism (cf. this vol., 82).

F. O. H.

Synthesis of the biological $l(-)$ -glyceryl- α -phosphoric acid. H. O. L. FISCHER and E. BAER (Naturwiss., 1937, 25, 589).— $d(+)$ -isoPropylidene-glycerol and $POCl_3$ in quinoline give the *Ba* α -phosphate and thence the natural $l(-)$ -glyceryl- α -phosphoric acid, $[\alpha]_D -1.45^\circ$ in 2N-HCl (Me_2 ether Me_2 ester, $[\alpha]_D -4.78^\circ$; Ag salt, $[\alpha]_D +1^\circ$ in dil. aq. NH_3). Embden's mechanism for the disproportion-

ation of triosephosphoric acids is thus proved. The following mechanism is probable: $\text{CO}_2\text{H}\cdot\text{C}(\text{OH})\cdot\text{CH}_2 + \text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}\cdot\text{PO}_3\text{H}_2 \rightarrow \text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H} + \text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{PO}_3\text{H}_2$. R. S. C.

Synthetic optically active glycerides. H. O. L. FISCHER and E. BAER (Naturwiss., 1937, 25, 588—589).—Ni-hydrogenation of isopropylidene-*d*-glyceraldehyde (from 1:2:5:6-diisopropylidenemannitol) gives *d*(+)- α -isopropylideneglycerol (I), b.p. 80—80.5°/12 mm., $[\alpha]_D^{20} +12.6^\circ$ (homogeneous), -1.6° in H_2O , $+11.09^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and thence the α -benzoate, b.p. 159—160°/10.5 mm., $[\alpha]_D^{18} +12.3^\circ$, -acetate, b.p. 85—86°/10—11 mm., $[\alpha]_D +3.24^\circ$, -laurate, b.p. 130—131°/0.002 mm., $[\alpha]_D^{21} +3.42^\circ$, -stearate, m.p. 43.5°, $[\alpha]_D^{20} +3.0$ to 3.5° (molten), $[\alpha]_D +1.9^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and -palmitate, m.p. 33—35°, $[\alpha]_D +2.48^\circ$ in $\text{C}_5\text{H}_5\text{N}$, $+4.38^\circ$ (molten), hydrolysed to *d*(+)-glycerol α -laurate, m.p. 53—54°, $[\alpha]_D -3.76^\circ$ in $\text{C}_5\text{H}_5\text{N}$, -stearate, m.p. 76—77°, $[\alpha] -3.58^\circ$ in $\text{C}_5\text{H}_5\text{N}$, -palmitate, m.p. 71—72°, $[\alpha]_D -4.37^\circ$, and -*p*-toluenesulphonate, m.p. 63—64°, $[\alpha]_D -7.3^\circ$ in $\text{C}_5\text{H}_5\text{N}$, which afford *d*(+)-glycerol α -laurate $\alpha'\beta$ -distearate, m.p. 67—68°, $[\alpha]_D 0^\circ$ in $\text{C}_5\text{H}_5\text{N}$, α -stearate $\alpha'\beta$ -dipalmitate, m.p. 62.5°, $[\alpha]_D 0^\circ$ in $\text{C}_5\text{H}_5\text{N}$ or CHCl_3 , α -palmitate $\alpha'\beta$ -dilaurate, m.p. 44°, $[\alpha]_D 0^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and α -*p*-nitrobenzoate $\alpha'\beta$ -dibenzoate, m.p. 77—78°, $[\alpha]_D -19.9^\circ$ in $\text{C}_2\text{H}_2\text{Cl}_4$. *d*(+)- α -isopropylideneglycerol α' -Me ether, b.p. 43—44°/10.5 mm., $[\alpha]_D +20.14^\circ$, is prepared. The *p*-nitrobenzoate of (I) gives *d*(+)-glycerol α -*p*-nitrobenzoate, m.p. 88—89°, $[\alpha]_D -17.1^\circ$ in EtOH , and thence the α' -*CPh*₃ ether α -*p*-nitrobenzoate, m.p. 138—139°, $[\alpha]_D -5.06^\circ$ in $\text{C}_2\text{H}_2\text{Cl}_4$, and α' -*CPh*₃ ether, m.p. 97—98°, $[\alpha]_D +2.8^\circ$ in $\text{C}_2\text{H}_2\text{Cl}_4$, *d*(+)- α -isopropylideneglycerol α' -*CPh*₃ ether, $[\alpha]_D -10.8^\circ$ in $\text{C}_2\text{H}_2\text{Cl}_4$, and *l*(-)-isopropylideneglycerol, $[\alpha]_D -12.6^\circ$. Unless otherwise stated, $[\alpha]$ are for the homogeneous substance. R. S. C.

Amorphous and crystallised oxide hydrates and oxides. XXXIII.—See A., I, 528.

Amplified distillation of binary aliphatic acid mixtures. W. N. AXE and A. C. BRATTON (J. Amer. Chem. Soc., 1937, 59, 1424—1425).—By amplified distillation (i.e., dilution with 10 vols. of hydrocarbon oil prior to distillation) 1:1 mixtures give 72% of pure EtCO_2H with 73% of pure $\text{Pr}^n\text{CO}_2\text{H}$ or 45.5% of pure $\text{pr}^n\text{CO}_2\text{H}$ with 16.5% of pure $\text{CH}_3\text{Pr}^n\text{CO}_2\text{H}$, the corresponding figures for ordinary distillation being 13.5, 50.4, 0, and 13.2%, respectively. The Dyer method of analysing the acids is modified.

R. S. C.

Preparation of acetic anhydride and homologues. V. M. RODIONOV, A. I. SMARIN, and T. A. ABLETZOVA (Chim. Farm. Prom., 1935, No. 2, 102—106).—A new method is based on the reaction $2\text{NaOAc} + \text{N}_2\text{O}_4 \rightarrow \text{Ac}_2\text{O} + \text{NaNO}_2 + \text{NaNO}_3$.

CH. ABS. (r)

Preparation of methyl methacrylate from isobutyric acid. J. S. SALKIND and I. F. MARKOV (J. Appl. Chem. Russ., 1937, 10, 1042—1044).— $\text{Pr}^n\text{CO}_2\text{H}$ and Cl_2 (60-watt lamp illumination) at an initial temp. of 50° yield $\text{CMe}_2\text{Cl}\cdot\text{CO}_2\text{H}$ (Me ester, b.p. 64—65°/55 mm., 128—129.5°/753 mm.) and

$\text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (Me ester, b.p. 85—90°/60 mm., 151—155°/750 mm.). These esters yield $\text{CH}_2\cdot\text{CMe}\cdot\text{CO}_2\text{Me}$ when boiled with quinoline in presence of quinol, and the acids give $\text{CH}_2\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ when distilled from active C. R. T.

Determination of oleic, linoleic, and linolenic acids in mixtures. E. DELVAUX (J. Pharm. Belg., 1936, 18, 101—105, 131—139, 153—159; Chem. Zentr., 1936, i, 3769).—The H_2 uptake of oleic acid (I), Me linoleate, linoleic acid (II), and mixtures with Et linoleate (III) in presence of a catalyst has been measured. The prep. of pure (I), (II), and linolenic acid is described and the absorption spectra of their pure Me esters and of pure (III) recorded. A method of determination based on $(\text{CNS})_2$ addition, hydrogenation, and absorption spectra is described.

H. N. R.

X-Ray and thermal examination of the glycerides. III. $\alpha'\alpha'$ -Diglycerides. T. MALKIN, M. R. EL SHURBAGY, and (in part) M. L. MEARA (J.C.S., 1937, 1409—1413; cf. A., 1934, 666; 1937, 17).—The $\alpha'\alpha'$ -diglycerides from $\alpha\alpha'$ -didecino to $\alpha\alpha'$ -dipentadecino exist in three solid forms (α , β' , and β) and from $\alpha\alpha'$ -dipalmitin to $\alpha\alpha'$ -distearin in two solid forms (α and β). The β -form is stable and high-melting, and separates from solvents; the lower-melting, metastable α -form separates first from the molten diglyceride, and rapidly changes into the β' -form (lower members) or the β -form (higher members), the β' -form rapidly changing to the β . The β' -form has m.p. intermediate between the α - and the β -forms. X-Ray examination shows that the crystals are built up of layers of double mols., with the hydrocarbon chains lying parallel on the same side of the glyceride mol. Suitable esterification of the monoglyceride with acid in presence of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, or with the acid chloride in $\text{C}_5\text{H}_5\text{N}$, yields the following (the m.p. given is that of the stable β -form): $\alpha\alpha'$ -*di*-, m.p. 44.5°, -*un*-, m.p. 49°, -*tri*-, m.p. 56.5°, -*penta*-, m.p. 68.5°, and -*hepta-decino*, m.p. 74.5°. J. D. R.

Association of certain fatty acids on the basis of their molecular polarisation. K. HRYNAKOWSKI and A. ZOCHOWSKI (Ber., 1937, 70, [B], 1927—1743).—The dielectric polarisation of the higher fatty acids increases with increasing concn. of their solutions in C_6H_6 in consequence of an increase in the mutual action of the hydrocarbon residues which diminishes with the increasing length of the hydrocarbon chain. The higher fatty acids do not show dipole character since their mols. associate in pairs to complexes of which the total moment is zero. The proportion of at. polarisation to displacement polarisation diminishes with lengthening of the chain. The elasticity of the mol. diminishes with increasing chain length in the homologous series of the fatty acids; the effect is probably a parallel to diminution in the mutual influence of the hydrocarbon residues.

H. W.

Oxidation of fats by per-acids. H. BÖHME and G. STEINKE (Ber., 1937, 70, [B], 1709—1713).—A weighed quantity of the fat or fatty acid in Et_2O is treated with the per-acid (usually $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{OH}$) (I) in Et_2O at the required temp. After given intervals the mixture is cooled to 0° and

an aliquot portion is mixed with KI; the liberated I is determined by $\text{Na}_2\text{S}_2\text{O}_3$. Oleic acid is oxidised somewhat more rapidly than elaidic acid. With octadecadienoic acid an inflexion in the graph occurs after consumption of about 50% of the calc. quantity of (I) owing to the presence of the conjugated double linking. The consumption of (I) corresponds quantitatively with the I val. for triolein, olive oil, and cacao butter. Sesame and poppy-seed oil require < and linseed oil considerably > the amount of (I) indicated by the I val. As far as can be judged at present, a parallelism appears between the diene and per-acid nos.

H. W.

Wax of white pine chermes. B. K. BLOUNT, A. C. CHITNALL, and H. A. EL MANGOURI (Biochem. J., 1937, 31, 1375—1378; cf. A., 1936, 1137).—The wax consists of *1-keto-n-triacontanoic acid*, m.p. 103.3—103.6° [*oxime* (I), m.p. 62.5°], esterified with *p-keto-n-hexatriaccontanol* (II), m.p. 102—102.5° (*acetate*, m.p. 84.2°; *oxime*, m.p. 78.5°), and a small amount of a *substance*, m.p. 78°, possibly a *n*-fatty acid. (I) with H_2SO_4 (100°; 1 hr.) gives a mixture of amides which with conc. HCl at 180° for 4 hr. yields arachidic acid (III), *n*-nonane- α -dicarboxylic acid, *n*-nonadecanamine hydrochloride (IV), and θ -amino-*n*-decoic acid hydrochloride. (II) with CrO_3 gives the corresponding keto-acid, the oxime of which, as in the case of (I), yields (III), (IV), *n*-pentadecane- α -dicarboxylic acid, and a trace of ξ -aminopalmitic acid hydrochloride.

W. McC.

Wool fat. A. HEIDUSCHKA and E. NIER (J. pr. Chem., 1937, [ii], 149, 98—106).—Wool fat is hydrolysed by KOH - EtOH and the saponifiable and unsaponifiable (I) matter are separated from one another by Et_2O . Cerotic acid, m.p. 78°, is obtained by fractional pptn. from the mixture of fatty acids and is purified through the Et ester and the Li salt. The *Pr*^a, m.p. 65.5°, *Pr*^b, m.p. 75°, *Bu*^b, m.p. 65.5°, and *amyl*, m.p. 63°, esters are new. Lanoceric acid, m.p. 102.5° (*Ag* salt; *Et* ester, m.p. 78°), is isolated by using its sparing solubility in Et_2O . Evidence of the presence of lanocerolactone was not obtained. (I) is separated by crystallisation and pptn. from MeOH and EtOH or their mixtures into a no. of fractions from which ceryl alcohol, *ischolesterol*, and cholesterol but not carnaubyl alcohol are isolated; other substances are present which could not be identified since they are smeary or resinous and retain these characteristics when oxidised.

H. W.

Racemiasse, an enzyme which catalyses racemisation of lactic acid.—See A., III, 311.

Polar group orientation in linear polymeric molecules. ω -Hydroxydecoic acids. W. B. BRIDGMAN and J. W. WILLIAMS (J. Amer. Chem. Soc., 1937, 59, 1579—1580).—Certain classes of polymerides of high mol. wt. do not give a measurable dispersion of ϵ in a frequency interval where this is expected from the chemical mol. wt. μ are determined for six polymerides of ω -hydroxydecoic acid (*M* 905—13,900). It appears that the μ is due mainly to rotation of the regularly spaced ester groups, for $\mu \propto \sqrt{M}$ and polarisation per g. of polymeride is independent

of *M*. The polymerides probably consist of flexible chains.

R. S. C.

Chemical constituents of lichens found in Ireland. *Lecanora sordida*, Th. Fr. G. KENNEDY, J. BREEN, J. KEENE, and T. J. NOLAN (Sci. Proc. Roy. Dublin Soc., 1937, 21, 557—566).—Extraction of the lichen with Et_2O followed by treatment with light petroleum gave a mixture of 65% of atranorin and 35% of chloratranorin, *roccellic acid* (I), m.p. 131°, $[\alpha]_D +17.4^\circ$ in EtOH , and an acid, $\text{C}_{24}\text{H}_{40}\text{O}_8\text{Cl}_2$, m.p. 258—260°, which gave a greenish-blue colour with $\text{EtOH}-\text{FeCl}_3$ (? thiophanic acid). Mannitol was also obtained from the residue. (I) is shown synthetically to be α -methyl- β -dodecylsuccinic acid, two forms, m.p. 131° and m.p. 81—82°, respectively. It gives a *Me*₂ ester, m.p. 28—29°, an *anil*, m.p. 57—58°, and a *derivative*, $\text{C}_{23}\text{H}_{35}\text{O}_4\text{N}_3$, m.p. 113—114°, with $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH-NH}_2$.

P. G. M.

Structure of glutaconic acid. A. I. VOGEL, W. L. GERMAN, and G. H. JEFFERY (Chem. and Ind., 1937, 804).—Determinations of the thermodynamic primary dissociation const. of glutaconic acid (I), m.p. 138°, at 25° by conductivity and of the two thermodynamic dissociation consts. by potentiometric titration with the quinhydrone electrode at 25° show the similarity of (I) and fumaric acid and provide evidence for the *trans* structure of the acid of m.p. 138°.

H. W.

Ethyl α -formyl- α' -hydroxyethylglutaconate. H. GAULT and M. COGAN (Compt. rend., 1937, 205, 151—153; cf. A., 1901, i, 361).— $\text{CHO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (as Na derivative) (1 mol.) with conc. HCl (1 mol.) and excess of MeCHO at -15° affords $\text{Et}_2\alpha$ -formyl- α' -hydroxyethylglutaconate which cannot be distilled (*Ac* derivative, b.p. 160—163°/0.7 mm.).

J. L. D.

Experiments towards the synthesis of isofenchone. I. Synthesis of $\beta\delta$ -dimethylpentane- $\beta\delta\epsilon$ -tricarboxylic acid. S. K. RANGANATHAN (J. Indian Chem. Soc., 1937, 14, 264—267; cf. this vol., 4).— β -Hydroxy- $\beta\delta\delta$ -trimethyladipolactone, m.p. 128—129°, is obtained by hydrolysis of the corresponding Et ester, which with KCN at 220° gives $\beta\delta$ -dimethylpentane- $\beta\delta\epsilon$ -tricarboxylic acid, m.p. 185—186° (cf. *loc. cit.*). The Et_3 ester of this when cyclised with $\text{Na-C}_6\text{H}_6$ and subsequently hydrolysed and decarboxylated gives isofenchocamphoronic acid [semicarbazone, m.p. 212—213° (decomp.) (cf. Bardhan *et al.*, this vol., 67)].

H. G. M.

Production of phosphoglyceric acid.—See A., III, 395.

Mol. wt. of racemic acid. E. W. BLANK (J. Chem. Educ., 1937, 14, 393).—This mol. wt. is twice that of the other forms of tartaric acid, and racemic acid should be represented by $2\text{C}_4\text{H}_6\text{O}_6 + 2\text{H}_2\text{O}$, not $\text{C}_4\text{H}_6\text{O}_6 + \text{H}_2\text{O}$.

L. S. T.

Enzymic determination of ascorbic acid.—See A., III, 406.

Stability of ascorbic and dehydroascorbic acids.—See A., III, 364.

Catalysis of Cannizzaro's reaction by active nickel and platinum. Application to aldoses.

M. DELÉPINE and A. HOREAU (Compt. rend., 1937, 204, 1605—1608).— CH_2O , $\text{Pr}^\text{c}\text{CHO}$, and PhCHO with NaOH and Ni at room temp. rapidly undergo the Cannizzaro reaction (cf. A., 1897, i, 504). Galactose similarly affords dulcitol and galactonic acid in good yield but not without Ni ; glucose and arabinose also react. With Pt as catalyst, the H_2 liberated in the oxidation reaction destroys some of the initial aldehyde. The reaction with Ni probably proceeds similarly although H_2 is not liberated, for crotonic acid added to the reaction mixture is partly reduced.

J. L. D.

Determination of formaldehyde and formic acid in the presence of one another. L. SPITZER (Annali Chim. Appl., 1937, 27, 292—296).— CH_2O is determined iodometrically by the Romijn method (A., 1897, ii, 166) and the total CH_2O and HCO_2H , bromometrically, by the Meulen (A., 1930, 1392) or a modified Oberhauser method (A., 1927, 475).

L. A. O'N.

Kinetics of polymeric aldehydes. VII. Velocity of hydrolysis of formaldehyde acetals. J. LÖBERING and A. FLEISCHMANN (Ber., 1937, 70, [B], 1713—1719).—Increase in size of the alkyl residue causes increase in the temp. coeff. of the hydrolysis of $\text{CH}_2(\text{OMe})_2$, $\text{CH}_2(\text{OEt})_2$, and $\text{CH}_2(\text{OPr}^\text{c})_2$. It appears therefore that the acetal yields a mol. of alcohol and a mol. of semiacetal which immediately, possibly owing to a very rapid intramol. process, gives CH_2O and a second mol. of alcohol. The coeffs. of these two reaction stages obey the Arrhenius law. The temp.-dependence of the dimeric product can be expressed by the same simple formula. Dimethoxydimethyl ether must therefore decompose thus: $\text{O}(\text{CH}_2\text{OMe})_2 + \text{H}_2\text{O} \rightarrow \text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{OH}$ (I) + MeOH ; (I) + $\text{H}_2\text{O} \rightarrow \text{CH}_2(\text{OH})_2 + \text{OMe}\cdot\text{CH}_2\cdot\text{OH}$ (II); (II) + $\text{H}_2\text{O} = \text{MeOH} + \text{CH}_2(\text{OH})_2$. Since these three stages are alike in character their summation coeff. must be determined by the same simple law. The rate of reaction is governed by that of the first step in a degree which increases with temp. Examination of the velocity coeff. of the initial members of the polymeric homologous series of Me_2 ethers shows that $\text{CH}_2(\text{OMe})_2$ decomposes most slowly and the dimeride has the highest hydrolysis const. At first the terminal group suddenly loses its influence on the total reaction. With increasing degree of polymerisation other influences make themselves felt; these cause a continuous decrease in the rate of depolymerisation with increasing chain length.

H. W.

Magnetism and polymerisation. II. Oxymethylene diacetates and polyoxymethylenes.—See A., I, 451.

Kinetics of polymeric aldehydes. VI. Formation and decomposition of polyoxymethylene. J. LÖBERING (Z. Elektrochem., 1937, 43, 638—643; cf. this vol., 228, 274).—The polymerisation of aq. CH_2O reaches an equilibrium state, and the degree of polymerisation of the pptd. polymeride, characteristic for the temp. and initial concn., increases with the temp. and with diminished initial concn. If the pptd. polymeride is removed from the solution it can be redissolved partly to form the equilibrium solution

with the depolymerised form, but the velocity of dissolution decreases with increasing degree of polymerisation. If the filtrate after removing the polymeride is kept at a lower temp. a further ppt. of a lower polymeride is formed. Catalysts increase the chain length of the polymeride, the effects being in the order $\text{H}_2\text{SO}_4 > \text{HCl} > \text{NaOH}$. Polymerisation probably occurs exclusively in solution and all polymerides are slightly sol.

J. W. S.

Hydration of unsaturated compounds. VI. Rate of hydration of *trans*-crotonaldehyde. Equilibrium between *trans*-crotonaldehyde and aldol in dilute aqueous solution. S. WINSTEIN and H. J. LUCAS (J. Amer. Chem. Soc., 1937, 59, 1461—1465).—*trans*- $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ (I) is reversibly hydrated to aldol (II) in 0.5N- HNO_3 or $-\text{HClO}_4$, equilibrium at 25° being with hydration of 47% of (I) and at 35° with hydration of 39% of (I). Energies of activation are 18.23 and 24.48 kg.-cal. for hydration and dehydration, respectively. Hydration and dehydration are first-order reactions, the former with respect to concns. of acid and (I), the latter with respect to concns. of acid and (II). The reactions in HClO_4 are 6—7% slower than in HNO_3 . $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ and *trans*- $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ are not appreciably hydrated in aq. HNO_3 at 25°.

R. S. C.

Detection and determination of small amounts of glucose in mixtures containing maltose. M. SOMOGYI (J. Biol. Chem., 1937, 119, 741—747).—The fermentation rate of a sugar solution at $\eta_{\text{H}} 7.2$ —7.4 is compared with that of a 1% maltose solution. In presence of glucose the fermentation proceeds faster than that of maltose. A quant. method is described, together with an alkaline reagent for the determination of slowly oxidised sugars.

J. L. C.

Disintegration of methylated glucoses in alkaline medium. N. ARIYAMA and T. KITASATO (J. Biochem. Japan, 1937, 25, 357—373).—The reducing properties of various mono- and poly-methylglucoses to various reagents and under various conditions were examined. The results of Sobotka (A., 1926, 1026) are generally confirmed. With mild treatment by alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ at 70°, the velocity of oxidation of 3- and 3:5:6-derivatives is higher initially but diminishes more rapidly than that of glucose (I); a similar relationship exists between the 2:3:4:6- and 2-derivatives. Transformation of 2-methylglucose occurs more readily than that of (I). With HIO_4 , production of aldehyde decreases with proximity of Me to $\text{C}_{(6)}$ and with the increase in no. of Me groups. Data for the equilibrium potentials of Me derivatives of (I) are given.

F. O. H.

Emulsin. XXX. Enzymic hydrolysis of 6-halohydrin- β -D-glucosides and of related compounds. B. HELFERICH, S. GRÜNLER, and A. GNÜCHTEL (Z. physiol. Chem., 1937, 248, 85—95; cf. A., III, 313).—The rate of hydrolysis by the emulsin (I) of sweet almonds of 6-substituted β -D-glucosides of vanillin decreases as the vol. of the substituent, as deduced by the methods of Biltz (A., 1931, 895) (OMe an exception) and Stuart (A., 1935, 432) (OH and OMe exceptions) and from the parachor (OH an exception), increases; thus $\text{H} > \text{OH}$

> F > Cl > Br > OMe > I. Acetobromoglucose 6-chlorohydrin with vanillin and KOH gives the *triacetate*, m.p. 141°, $[\alpha]_D^{25}$ -53.0° in CHCl₃, of *vanillin-β-d-glucoside 6-chlorohydrin*, m.p. 162—164°, $[\alpha]_D^{25}$ -85.5° in C₅H₅N. The *6-bromohydrin*, m.p. 181—182°, $[\alpha]_D^{25}$ -110° in aq. EtOH [*triacetate* (II), m.p. 146—148°, $[\alpha]_D^{25}$ -58.1° in CHCl₃], and *vanillin-β-d-isorhamnoside* (III), m.p. 162—165°, $[\alpha]_D^{25}$ -85.2° in H₂O (*triacetate*, m.p. 179—181°, $[\alpha]_D^{25}$ -31.5°), are obtained in the same way, and (II) at 100—120° for 3 hr. with NaI in COMe₂ gives the *triacetate*, m.p. 136—138°, $[\alpha]_D^{25}$ -67.3° in CHCl₃, of the *6-iodohydrin*, m.p. 205—207° (decomp.), $[\alpha]_D^{25}$ -116° in C₅H₅N. (III) is less rapidly hydrolysed by (I) than is the corresponding glucoside. *Phenol-β-d-glucoside 6-fluorohydrin* has m.p. 148—149°, $[\alpha]_D^{25}$ -79° in H₂O.

W. McC.

Ketone sugar series. VIII. Structure of *l*-sorbose penta-acetate. F. B. CRAMER and E. PACSU (J. Amer. Chem. Soc., 1937, 59, 1467—1469; cf. this vol., 325).—Sorbose tetra-acetate has m.p. 100—101.5°, $[\alpha]_D^{25}$ -19.4°, and contains no solvent. With Ac₂O and ZnCl₂ at room temp. or 50° it gives the penta-acetate (I), which is a derivative of ketosorbose, since with H₂-Pt, best in Et₂O at 4 atm., it yields a syrup, whence by acetylation 60% of *l*-iditol and 40% of *d*-sorbitol hexa-acetates are obtained. *l*-Iditol is readily prepared by this method. Ketone reagents are without effect on (I); addition of a little NaOH to (I) in COMe₂ gives a deep yellow solution, which after neutralisation reduces KMnO₄.

R. S. C.

History of the rotatory power of sucrose. D. SIDERSKY (Bull. Assoc. Chim. Sucr., 1937, 54, 413—424).—An account is given of the more important determinations, and results are summarised in a table showing vals. of $[\alpha]_D^{25}$ for different concns. of sucrose.

J. H. L.

Sugar osazones and their anhydrides. E. E. PERCIVAL and E. G. V. PERCIVAL (J.C.S., 1937, 1320—1325).—Lactosephenylosazone is acetylated (Ac₂O-C₅H₅N) to the *hepta-acetate*, m.p. 105—110°, $[\alpha]_D^{25}$ +27° in CHCl₃, which with NaOH in aq. COMe₂ affords anhydrolactosephenylosazone, m.p. 231—232°, identical with that of Diels and Meyer (A., 1935, 1225), converted by acetylation into *anhydrolactosephenylosazone penta-acetate*, m.p. 115—117°, $[\alpha]_D^{25}$ -102° in COMe₂. Similar acetylation of maltosephenylosazone yields the *hepta-acetate*, m.p. 162°, $[\alpha]_D^{25}$ +41° in CHCl₃, deacetylated (NaOH in aq. COMe₂) to two products, C₂₄H₃₀O₈N₄ (I), m.p. 245—246°, $[\alpha]_D^{25}$ +58° in C₅H₅N, and C₂₄H₃₄O₁₀N₄ (II), m.p. 194°, $[\alpha]_D^{25}$ +160° in C₅H₅N. Acetylation of (I) yields an amorphous *penta-acetate*, $[\alpha]_D^{25}$ +90.7° in COMe₂, whilst (II) affords an amorphous *penta-acetate*, m.p. 110—112°, $[\alpha]_D^{25}$ +150° in COMe₂. By acetylation (Ac₂O-C₅H₅N) of the appropriate osazone, *d*-xylosazone *triacetate*, m.p. 116—117°, $[\alpha]_D^{25}$ -46° in CHCl₃, *l*-arabinosazone *triacetate*, m.p. 114°, $[\alpha]_D^{25}$ +5° in CHCl₃, and *l*-rhamnosazone *triacetate*, m.p. 75°, $[\alpha]_D^{25}$ +52° in CHCl₃, are produced; attempted deacetylation of these led to non-cryst. products. Monoanhydro-glucosazone and -galactosazone when acetylated afford *monoanhydroglucosazone diacetate*, m.p. 70°, $[\alpha]_D^{25}$ -125° in

CHCl₃, and *monoanhydrogalactosazone diacetate*, m.p. 86°, $[\alpha]_D^{25}$ +64° in CHCl₃, respectively. *Fructosephenylmethylhydrazone*, m.p. 170°, $[\alpha]_D^{25}$ -253° in C₅H₅N-EtOH (4 : 6) (from fructose and NPhMe-NH₂ in EtOH-aq. AcOH), when acetylated yields a *penta-acetate*, m.p. 121°, $[\alpha]_D^{25}$ +86.5° in CHCl₃, whilst the phenylmethylsazone affords a *tetra-acetate*, m.p. 128°, $[\alpha]_D^{25}$ -435° in CHCl₃, -236° in 95% EtOH. Glucosephenylhydrazone yields a *penta-acetate*, m.p. 152°, $[\alpha]_D^{25}$ -10.4° in C₅H₅N, and glucosephenylmethylhydrazone a *penta-acetate*, m.p. 113—114°, $[\alpha]_D^{25}$ +157° in CHCl₃. There is little evidence to differentiate between the *N*-Ac and the *O*-Ac structures in the acetates formed.

J. D. R.

Titrimetric determination of sugar.—See A., III, 410.

***d*- and *l*-Borneolglucosides.** W. LIPSCHITZ and E. BÜDING (Compt. rend., 1937, 205, 58—60; cf. A., 1909, i, 365).—Acetobromoglucose, m.p. 87—89°, $[\alpha]_D^{25}$ +195.5° in Et₂O (cf. A., 1917, i, 467), with Ag₂CO₃ and *d*-borneol affords *d*-borneolglucoside tetra-acetate, m.p. 131.5° (lit., 119—120°), $[\alpha]_D^{25}$ -20.9° in C₆H₆, hydrolysed by 0.4*N*-Ba(OH)₂ at 60° to *d*-borneol-β-glucoside, m.p. 154—155° (lit., 134—136°), $[\alpha]_D^{25}$ -15.2° in EtOH, H₂O content, 5.4% (lit., 4.54%), but after crystallisation from H₂O it was 4.35%. Similarly prepared, *l*-borneolglucoside tetra-acetate has m.p. 118—119.5°, $[\alpha]_D^{25}$ -52.7° in C₆H₆, and *l*-borneol-β-glucoside, m.p. 135—136°, $[\alpha]_D^{25}$ +55.6° in 95% EtOH, H₂O content 4.45%.

J. L. D.

Soluble dextrans and the constitution of starch. K. MYRBACK (Current Sci., 1937, 6, 47—50).—A review.

Are dextrans fermentable? H. HAEHN, M. GLAUBITZ, and W. GROSS (Z. Spiritusind., 1937, 60, 197—198, 206, 208).—A detailed account of work already noted (this vol., 370).

I. A. P.

Molecular structure of canna starch. W. Z. HASSID and W. H. DORE (J. Amer. Chem. Soc., 1937, 59, 1503—1508).—Hydrolysis of the fully methylated starch, followed by quant. separation of the cleavage products into 2 : 3 : 4 : 6-tetramethyl- and 2 : 3 : 6-trimethyl-glucose, shows the starch mol. to contain about 27 anhydroglucose units. These probably form chains, which are bound by primary valencies, and are associated by secondary valencies to form a colloidal unit, [(C₆H₁₀O₅)_m]_n, where *n* is the no. of associated chains and *m* the no. of glucose units in the chain (26—30). A starch triacetate, containing a single unaggregated mol., has been prepared directly from canna starch without special preliminary disaggregation.

E. S. H.

Glycogen. VI. Molecular structure of horse muscle-glycogen. D. J. BELL (Biochem. J., 1937, 31, 1683—1691; cf. A., 1937, III, 7).—Acetylation followed by simultaneous deacetylation and methylation of the glycogen (I) affords a methylated (I), $[\alpha]_D^{25}$ +208° in CHCl₃, +207° in H₂O, org. P 0.018%, which, on hydrolysis and fractional distillation of the methylated hydrolysate, afforded 10% of 2 : 3 : 4 : 6-tetramethylmethylglucoside and nearly 15% of dimethylmethylglucoside (II). Hence (I) has a min.

chain length of 11–12 glucose units. The bearing of the production of (II) on the possible aggregation of relatively small "unit-chains" is discussed.

F. O. H.

Action of liquid ammonia on cellulose fibres. Formation of ammonia-cellulose I, ammonia-cellulose II, and cellulose III. K. HESS and J. GUNDERMANN (Ber., 1937, 70, [B], 1788–1799).—In contact with liquid NH_3 cellulose forms two ammoniates dependent on temp.; these are mutually interconvertible between -20° and -30° . *Ammonia-cellulose* II (I), the form stable at the lower temp., has a fibre period of $15.20 \text{ \AA} = 3 \times 5.07 \text{ \AA}$ and trigonal symmetry. Probably the fibre axis is a trigonal screw axis. The dimensions of the usually-hexagonal, elementary cell are $a = c = 14.50$, $b = 14.20 \text{ \AA}$, $\beta = 60^\circ$, cell vol. = 2764 \AA^3 . The probable composition is $\text{C}_6\text{H}_{10}\text{O}_5(\text{NH}_3)_6$. *Ammonia-cellulose* I (II), the variety more stable at the higher temp., has fibre period $10.30 = 2 \times 5.15 \text{ \AA}$. A satisfactory interpretation of its Röntgen diagram cannot yet be given. It is not yet possible to decide whether (I) and (II) are different modifications with the same chemical composition or ammoniates with different NH_3 content. Decomp. of (I) or (II) leads to a new modification, *cellulose* III (III). Its Röntgen diagram resembles that of hydrocellulose (IV), having, as has natural cellulose (V), a fibre period of 10.3 \AA . In contrast with (IV), (III) passes at 200° largely into (V) of which it is regarded as an unstable modification. Except for small differences the changes above described occur similarly with natural or mercerised cellulose fibres. It is therefore possible through (III) to effect a re-conversion of (IV) into (V). H. W.

Available surface of cellulose.—See A., I, 442.

Reaction metal hydroxide solution-cellulose fibre. III. Transformation reactions in 0–10% sodium hydroxide solutions of sodium celluloses obtained in highly concentrated sodium hydroxide solutions. W. SCHRAMEK and O. SUCCOLOWSKY (Kolloid-Z., 1937, 80, 129–138; cf. A., 1935, 1074).—Published work is critically discussed and supplementary data have been obtained by X-ray analysis of the products. The product of direct reaction of cellulose with 10–20% aq. NaOH is Na-cellulose I (period 10–20 \AA), and with >20% NaOH is Na-cellulose II (15 \AA). By dilution of these liquors the products are Na-cellulose IV (10 \AA) and Na-cellulose III (15 \AA), respectively, both of which can be further transformed into cellulose hydrate. Na-cellulose III is an intermediate, unstable modification (10 \AA). The conditions of interconversion of these products are described. E. S. H.

Oxycellulose. J. DUMAS (Rev. Gén. Mat. Col., 1937, 41, 381–382).—The intensity of colour and its tendency towards grey produced by the action of Nessler's reagent on cellulose increases with the proportion of oxycellulose; the aldehydic group of the latter causes the production of Hg_2I_2 which passes into $\text{HgI}_2 + \text{Hg}$. H. W.

Polyamines. III. Preparation of unsymmetrical amines of the type $\text{NHR} \cdot \text{C}_2\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_4 \cdot \text{NH}_2$ and $\text{NH}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{NH} \cdot \text{C}_3\text{H}_6 \cdot \text{NH}_2$, and the action of ammonia on di-*p*-toluenesulphonylbis-(β -chloro-

Q^* (A., II.)

ethyl)ethylenediamine. D. H. PEACOCK and Y. S. GWAN (J.C.S., 1937, 1468–1471; cf. A., 1934, 1207; 1936, 1493).—*p*-Toluenesulphonbenzyl- β -hydroxyethylamide with SOCl_2 in $\text{C}_6\text{H}_5\text{N}$ yields *p*-toluenesulphonbenzyl- β -chloroethylamide (I), m.p. 69° , which with $(\text{CH}_3\text{NH}_2)_2$ (II) affords a mixture of the dihydrochloride, m.p. 149 – 150° , of *N*-*p*-toluenesulphonbenzylamidoethylthylenediamine, and the hydrochloride m.p. 141 – 142° , of *NN'*-bis-(β -*p*-toluenesulphonbenzylamidoethyl)thylenediamine [$\text{p-C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{N}(\text{CH}_2\text{Ph}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot]_2$. *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{NEtNa}$ and $\text{Cl} \cdot [\text{CH}_2]_2 \cdot \text{OH}$ or $(\text{CH}_2)_2\text{O}$ yield *p*-toluenesulphon-(β -hydroxyethyl)ethylamide, converted (SOCl_2 - $\text{C}_5\text{H}_5\text{N}$) into *p*-toluenesulphon-(β -chloroethyl)ethylamide, m.p. 67° , which, treated successively with (II) in $\text{C}_6\text{H}_5\text{N}$ and *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{Cl}$, gives the tri-*p*-toluenesulphonyl derivative, m.p. 203° , of *N*- β -aminoethyl-*N'*-ethylethylenediamine. *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{NHNa}$ with $\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{OH}$ yields crude *p*-toluenesulphon- γ -hydroxypropylamide, converted (SOCl_2 - $\text{C}_5\text{H}_5\text{N}$) into *p*-toluenesulphon- γ -chloropropylamide, m.p. 53° , which with (II) affords the dihydrochloride, m.p. 202° , of *N*-(γ -*p*-toluenesulphonamido-propyl)thylenediamine, and *NN'*-bis-(γ -*p*-toluenesulphonamido-propyl)thylenediamine dihydrochloride. (I) with $\text{NH}_2 \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$ gives the trihydrochloride, m.p. 205° , of β -(*p*-toluenesulphonamidoethyl)trimethylethylenediamine, and the dihydrochloride, m.p. 215° , of *NN'*-bis-(β -*p*-toluenesulphonamidoethyl)trimethylethylenediamine. (*p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot)_2$ and $(\text{CH}_2)_2\text{O}$ with $\text{EtOH} \cdot \text{NaOEt} \cdot \text{C}_6\text{H}_5$ afford a mixture of *NN'*-di-*p*-toluenesulphonyl-*NN'*-bis-(β -hydroxyethyl)thylenediamine (IV), m.p. 144° , and di-*p*-toluenesulphonyl-*N*- β -hydroxyethylthylenediamine (V), which is converted (SOCl_2) into di-*p*-toluenesulphonyl-*N*- β -chloroethylthylenediamine, m.p. 111° , transformed by Na in EtOH or by (II) into 1:4-di-*p*-toluenesulphonylpiperazine, m.p. 291° (cf. A., 1934, 1207). With SOCl_2 - $\text{C}_5\text{H}_5\text{N} \cdot \text{CCl}_4$, (IV) yields *NN'*-di-*p*-toluenesulphonyl-*NN'*-bis-(β -chloroethyl)thylenediamine, m.p. 145° , which with $\text{NH}_3 \cdot \text{EtOH}$ gives *NN'*-di-*p*-toluenesulphonyl-*NN'*-bis-(β -aminoethyl)thylenediamine (VI), m.p. 134° (dihydrochloride, m.p. 243°), and 1:4-di-*p*-toluenesulphonyl-1:4:7-triazacyclononane, m.p. 218° (hydrochloride, m.p. 289°). Hydrolysis of (VI) (conc. H_2SO_4) affords *NN'*-bis-(β -aminoethyl)thylenediamine. *p*-Toluenesulphon- β -chloroethylamide and $\text{NH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2)_2$ in EtOH yield the trihydrochloride, m.p. $>360^\circ$, of *p*-toluenesulphonyl-*NN'*-bis-(β -aminoethyl)thylenediamine. J. D. R.

isoPropylmethyleimine, b.p. 220° .—See A., I, 501.

Synthesis of amino-acids by condensation of amines with aldehydes and hydrocyanic acid. Mechanism of synthesis, and application to synthesis of alkamino-acids. B. A. RASCHKOVAN (Trav. Inst. Chim. Charkov, 1936, 2, 41–79).—The mechanism of the Strecker reaction is discussed, and an electronic mechanism is proposed. Published work (this vol., 309) is described. R. T.

Combination of sugars with amino-acids in a current of oxygen. B. BAUMINGER and F. LIEBEN (Biochem. Z., 1937, 292, 92–97).—At initial p_{H} 8 and 70° the amount of CO_2 liberated by a current of

O₂ from a mixture of glucose (I) and glycine (II) is > that liberated from (I) alone, whilst the amount of acid (partly an increased amount of lactic acid) produced and the amount of (I) decomposed are increased, the effects being most pronounced when the mol. ratio (I) : (II) is 1.5 : 1. Liberation of CO₂ is favoured by alkaline media in the case of the mixture and by acid media in that of (I), so that when the initial p_H is 7.2 the reverse holds. The magnitude of the changes is increased by addition of Fe⁺⁺⁺ but the total amount of (I) decomposed remains small. (II) alone is but slightly affected (deaminated) by the O₂ current. Probably combination of (I) with (II) occurs. W. McC.

Interaction of α -amino-acids and peptides with sugars in aqueous solution. M. FRANKEL and A. KATCHALSKY (Biochem. J., 1937, 31, 1595—1604).—The interaction of α -NH₂-acids and peptides with various monoaldoses and aldodisaccharides is followed by the lowering of p_H consequent on the disappearance of NH₂-groups during the reaction. The α -NH₂ appear to be the dominating factor. The reaction takes place over a p_H range of 4.5—11 and has an optimum zone. In a strongly alkaline medium ($p_H > 10$) a second reaction predominates, the nature of which is discussed. P. W. C.

Alkamino-acids (hydroxyalkamino-acids); their synthesis and reactions. A. I. KIPRIANOV (Trav. Inst. Chim. Charkov, 1935, 1, 39—51).—A review of published papers. R. T.

Amino-acids and related compounds. X. Electrolytic oxidation of aspartic acid and malonic acid. Y. TAKAYAMA and S. MIDUNO. XI. Formation of aldehydes by the electrolytic oxidation of α -amino-acids. Y. TAKAYAMA, T. HARADA, and S. MIDUNO (Bull. Chem. Soc. Japan, 1937, 12, 338—341, 342—349).—X. Aspartic acid in N-H₂SO₄ oxidised at a PbO₂ anode gives, at 35°, HCO₂H, CH₂(CO₂H)₂, (·CH₂·CO₂H)₂, NH₃, and CO₂ and at 100° the same products with MeCHO instead of CH₂(CO₂H)₂, which is similarly oxidised at 35° to HCO₂H and CO₂ and at 100° to HCO₂H and a little CH₂O. The mechanism of the oxidation is presumed to be through CHO·CH₂·CO₂H.

XI. The oxidation of glycine, alanine, valine, and leucine (cf. A., 1933, 1127), repeated at 100°, the volatile products being distilled off during electrolysis, gives rise to the corresponding aldehydes (NH₂·CHR·CO₂H → R·CHO). MeCHO can be isolated from the oxidation products of alanine at 35° when the volatile products are removed by bubbling air through the cell. F. R. G.

Formation of histamine from histidine by catalytic oxido-reduction. P. HOLTZ (Naturwiss., 1937, 25, 589).—Alternate passage of O₂ (0.5—1 min.) and H₂ (2—3 min.) into 10 c.c. of neutral buffered 0.1% aq. *l*-histidine (I) hydrochloride in the presence of 1—2 mg. of Pd-black for 30 min. gives 2 × 10⁻⁵ g. of histamine (II), determined biologically. The formation of (II) from (I) in the presence of ascorbic acid and SH-compounds is due to oxidation by peroxidic intermediates, decarboxylation, and finally reduction. R. S. C.

Peptides of aminomalonic acid and of *l*(+)- $\alpha\beta$ -diaminopropionic acid. F. SCHNEIDER (Biochem. Z., 1937, 291, 328—339; cf. this vol., 233).—The hydrochloride of Et₂ aminomalonate (I) with CH₂Ph·COCl in presence of MgO gives the corresponding carbobenzyloxy-derivative, which with KOH in EtOH gives the *Et* ester, m.p. 66° [chloride (II), m.p. approx. 37°], of carbobenzyloxylaminomalonic acid. (II) with the *Et* ester of glycine (III) gives the *Et*₂ ester, m.p. 114°, of the carbobenzyloxy-derivative, m.p. 145° (decomp.), of the corresponding peptide, m.p. 181° (decomp.). (I) with the chloride (IV) of carbobenzyloxyglycine gives the *Et*₂ ester, m.p. 99°, of the carbobenzyloxy-derivative, m.p. 136° (decomp.), of glycylaminomalonic acid, decomp. > 220°, and, with the chloride of carbobenzyloxy-*l*-alanine, the *Et*₂ ester (V), m.p. 121°, of the carbobenzyloxy-derivative, m.p. 140° (decomp.), of *l*-alanylmalonic acid, decomp. > 225°, [α]_D²⁵ + 13.79° ± 0.3° in H₂O. (V) with NH₃ in MeOH gives the carbobenzyloxy-derivative, m.p. 220°, of the diamide, m.p. 171° (decomp.), [α]_D²⁵ + 3.96° ± 0.3° in H₂O. (II) with (III) gives the *Et* ester, m.p. 133°, of the carbobenzyloxy-derivative (amide, m.p. 175°) of aminomalonylglycine (amide, decomp. 201°). Me β -carbobenzyloxydiaminopropionate hydrochloride with (IV) in presence of MgO gives the *Me* ester, m.p. 91°, of α -carbobenzyloxyglycyl- β -carbobenzyloxydiaminopropionic acid, converted in the usual manner into the sulphate, [α]_D²⁵ - 16.50° ± 0.3° in H₂O, of α -glycyl-*l*-diaminopropionic acid. Me *l*-diaminopropionate with (IV) gives the *Me* ester, m.p. 133°, of $\alpha\beta$ -dicarbobenzyloxyglycyl-*l*-diaminopropionic acid, which yields the sulphate, [α]_D²⁵ - 1.09° ± 0.15° in H₂O, of $\alpha\beta$ -diglycyl-*l*-diaminopropionic acid in the usual manner. Dicarbobenzyloxy-*l*-diaminopropionyl chloride with (III) *Et* ester gives the *Et* ester, m.p. 145—146°, of dicarbobenzyloxy-*l*-diaminopropionylglycine, m.p. 160°, converted in the usual way into *l*-diaminopropionylglycine sulphate, [α]_D²⁵ + 30.90° ± 0.3° in H₂O. W. McC.

Diamino-acid, canavanine, and monoamino-acid, canaline. M. KITAGAWA (J. Biochem. Japan, 1937, 25, 23—41; cf. A., 1936, 320, 1236).—The prep. and properties of canavanine (I), C₅H₁₂O₃N₄ [picrate, m.p. 220°; dipicrate, m.p. 163—164°; sulphate, m.p. 172° (decomp.), [α]_D²⁵ + 19.41° in H₂O; Bz₃ derivative, m.p. approx. 86°; Cu salt, (I)₂Cu, m.p. 205—207° (decomp.); CuSO₄ derivative, (I)₂CuSO₄, m.p. approx. 190° (decomp.); *Me* ester dihydrochloride, m.p. 166—167° (decomp.)], are described. Hydrolysis by canavanase (pig's liver) affords (75% yield) canaline (II), C₄H₁₀O₃N₂ (A., 1934, 61), [α]_D²⁵ - 8.31 in H₂O [flavinate, m.p. 211° (decomp.); dipicrate, m.p. 193—194° (decomp.); hydrochloride, (II)₂·1.5HCl, m.p. 166° (decomp.); sulphate, (II)₂·0.75H₂SO₄, m.p. 97° (decomp.); Cu salt, (II)₂Cu; *Et* ester hydrochloride, m.p. 172—173° (decomp.)], the synthesis and constitution of which are discussed. The distribution and biological properties of (I) are reviewed. F. O. H.

Canavanine. VIII. M. KITAGAWA and J. TSUKAMOTO (J. Agric. Chem. Soc. Japan, 1937, 13, 601—612).—Canavanine when heated in aq. EtOH easily

loses NH_3 giving *deaminocanavanine*, $\text{C}_5\text{H}_9\text{O}_3\text{N}_3$. This gives a Sakaguchi reaction for guanido-fatty acids, forms a *Cu* salt and an *ester* with EtOH , gives a negative ninhydrin reaction, and on prolonged hydrolysis with acid yields canaline. A provisional structure is given. J. N. A.

α -Guanidoglutaric acid, a possible precursor of creatine. K. THOMAS and A. AKAO (J. Biochem. Japan, 1937, 25, 339—356).— α -Guanidoglutaric acid, m.p. 150—152° (cf. Kapfhammer and Müller, A., 1934, 876) [*anhydride*, m.p. 245° (decomp.); *Me* ester *hydrochloride*, m.p. 135°; *oxalate*, m.p. 209° (decomp.); *Me* ester *oxalate*, m.p. 144—146°; *phenacyl* ester, m.p. 246°, and the following related compounds were prepared: *diphenacyl* ester, *anhydride*, and *phenacyl* ester *anhydride* of α -ureidoglutaric acid, m.p. 136.5° (decomp.), 186°, and 145°, respectively, and *phenacyl ureidoacetate*, m.p. 162°. The constitutions of some of these compounds and their bearing on the formation of creatine in the organism are discussed. F. O. H.

Constitution of octopine, a nitrogenous substance from the muscle of *Octopoda*. I. Properties and degradation. II. Synthesis. III. Stereochemistry. S. AKASI (J. Biochem. Japan, 1937, 25, 261—280, 281—290, 291—298).—I. Octopode muscle yields arginine and 0.036% of *octopine* (I), $\text{C}_9\text{H}_{18}\text{O}_4\text{N}_4$, m.p. 281—282°, $[\alpha]_D^{25} + 20.94^\circ$ in H_2O [*picrate*, m.p. 225°; *flavinate*; $\text{Cu}(\text{NO}_3)_2$ salt, m.p. 247°]. (I) gives negative Jaffé and ninhydrin reactions and contains no $\text{NH}_2\text{-N}$. Hydrolysis with aq. $\text{Ba}(\text{OH})_2$ affords $\text{CO}(\text{NH}_2)_2$ and *octopinic acid* (II), $\text{C}_8\text{H}_{14}\text{O}_4\text{N}_2$, m.p. 270—271° (decomp.), $[\alpha]_D^{20} + 18.48^\circ$ in H_2O (*Cu* salt, m.p. 237°; *Bz* derivative, m.p. 213—214°), containing 2 CO_2H and NH_2 . Oxidation of (I) by BaMn_2O_8 yields γ -guanidobutyric acid. Condensation of $\text{CN}\cdot\text{NH}_2$ with (II) affords (I).

II. *d*-Arginine (III) with *dl*- or *L*- $\text{CHMeBr}\cdot\text{CO}_2\text{H}$ in dil. aq. NaOH at 37° for 72 hr. affords (I). Thus (I) is $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ and (II) $\text{NH}_2\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. (III) with $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ yields the isomeric δ -guanido- α -(β -carboxyethylamino)valeric acid (IV), m.p. 275—276°, $[\alpha]_D^{25} + 23.18^\circ$ in H_2O [*picrate*, m.p. 225°].

III. (III) with *dl*- or *d*- $\text{CHMeBr}\cdot\text{CO}_2\text{H}$ yields *isooctopine* (V), $\text{C}_9\text{H}_{18}\text{O}_4\text{N}_4\cdot 2\text{H}_2\text{O}$, m.p. 158—159° [mixture with (I), m.p. 158°], $[\alpha]_D^{20} + 25.77^\circ$ in H_2O [*picrate*, m.p. 198°], oxidised to (II). Application of the method of Lutz and Jirgensons (A., 1931, 943) to (I), (IV), and (V) is described and the configuration of the substances discussed. F. O. H.

Relations of thiocarbamide, cysteine, and the corresponding disulphides. G. TOENNIES (J. Biol. Chem., 1937, 120, 297—313).—Cysteine (I) oxidised by dithioformamidine (II) gives, contrary to Pirie (A., 1933, 1018), *S*-(guanythio)-*L*-cysteine, $\text{NH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{S}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ (III), isolated as its *hydrochloride*, decomp. 150—155°, $[\alpha]_D^{25} - 110^\circ$. Cystine (IV) with (II) also yields (III) when $\text{CS}(\text{NH}_2)_2$ is present. The influence of varying amounts of $\text{CS}(\text{NH}_2)_2$ on the phosphotungstate determination of (I) and (IV) is tabulated. F. R. G.

Oxidation of thiol compounds by hydrogen peroxide in presence of inorganic catalysts. II. Oxidation of cystine by means of hydrogen peroxide in presence of vanadic acid sol. J. C. GHOSH and B. C. KAR (J. Indian Chem. Soc., 1937, 14, 249—253).—Cysteic acid is the main product. The effects of varying temp., concn. and p_H on the velocity of the reaction have been studied. F. J. G.

Synthesis of hexocystine and hexomethionine and their physiological availability. C. B. JONES and V. DU VIGNEAUD (J. Biol. Chem., 1937, 120, 11—20).—The condensation product of Et sodio-phthalimidomalonate with $\text{Br}\cdot[\text{CH}_2]_4\cdot\text{Br}$ in 95% EtOH with H_2S in NaOH and subsequent hydrolysis gives $\epsilon\epsilon'$ -dithio- $\alpha\alpha'$ -diaminodihexoic acid (*hexocystine*) *hydrochloride* (I), the solution of which with Na in NH_3 gives with CH_2PhCl , *S*-benzylcysteine, m.p. 240—242° (decomp.) (*N*-formyl derivative, m.p. 103—104°), and with MeI , ϵ -methylthiol- α -aminohexoic acid (*hexomethionine*) (II), m.p. 276—278° (decomp.) (*benzenesulphonyl* derivative, m.p. 86—87°). Neither (I) nor (II) produced any alteration in the growth curves of rats on a cystine-deficient diet (cf. A., 1935, 389). F. R. G.

Condensation of cyanoacetamide with formaldehyde. II. Rate of reaction under differing conditions. T. ENKVIST (J. pr. Chem., 1937, [ii], 149, 65—84).—The reaction between $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ and CH_2O at 20° (followed by periodical determination of CH_2O) is bimol. and in absence of any sp. catalyst the rate is $\propto [\text{OH}^-]$. In alkaline solutions the change proceeds very rapidly. NH_4Cl , $\text{C}_5\text{H}_5\text{N}$, HCl , peroxides, and HCO_2K have no appreciable catalytic action whereas semicarbazide *hydrochloride* appears to cause an initial and transient acceleration. Piperidine *hydrochloride* produces such marked acceleration that its effect can scarcely be ascribed to the different change of the position of mesomerism in the anion induced by a different cation. A more probable explanation is indicated by the scheme: $\text{C}_5\text{H}_{10}\text{NH} + \text{CH}_2\text{O} = \text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2\cdot\text{OH}$ (I); (I) = $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2^+$

(II) + OH^- ; $\text{CN}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2^- + (\text{II}) \rightarrow \text{NH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CH}_2\cdot\text{NC}_5\text{H}_{10}$ (III); (III) + $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2 = \text{CH}_2[\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2]_2 + \text{C}_5\text{H}_{10}\text{NH}$. H. W.

Limits and velocity of formation of pyromucanilide. B. Z. AMITIN and S. A. LITKEVITSCH (Trav. Inst. Chim. Charkov, 1935, 1, 33—37).—The velocity of reaction of pyromucic acid with NH_2Ph is $>$ with NH_3 , and the yield of anilide is $>$ that of amide. The reaction is favoured by high temp. R. T.

Applications of the nitro-ferrocyanide [nitroprusside] reaction: new formula for carbamide. W. R. FEARON (Analyst, 1937, 62, 586—589).—Carbamide (I) is oxidised at room temp. with neutral aq. Br to a substance (II) which gives a reaction with Na nitroprusside given by ketonoid compounds containing an NH linked on both sides to C . (II) may be $\text{NH} > \text{CO}$, or hydrazo-ketone, since it is decomposed into N_2H_4 and CO_2 by warming with aq. $\text{Ba}(\text{OH})_2$. Possibly (I) exists in aq. solution as $\text{NH} > \text{CH}\cdot\text{OH}$ (hydrazo-carbinol). E. C. S.

Asymmetrical arylalkylcarbamides. II. Preparation, physical properties, and hypnotic effects. J. S. BUCK, A. M. HJORT, E. J. DE BEER, C. W. FERRY, and W. S. IDE (J. Pharm. Exp. Ther., 1937, 60, 369—386; cf. A., 1935, 1488).—The following new *as*-carbamide derivatives have been prepared from the corresponding *sec.* amines by the method of Buck and Ferry (A., 1936, 829): *o*-, m.p. 95°, *m*-, m.p. 86°, and *p*-anisyl-, m.p. 116°, *o*-, m.p. 63°, *m*-, m.p. 88.5°, and *p*-phenetyl-, m.p. 110°, *n*-propyl-, *m*-tolyl-, m.p. 66°, *o*-, m.p. 90°, and *p*-anisyl-, m.p. 106°, *o*-, m.p. 56°, and *p*-phenetyl-, m.p. 90°, *n*-butyl-, *m*-tolyl-, m.p. 67°, *o*-, m.p. 53°, and *p*-anisyl-, m.p. 94°, and *p*-phenetyl-, m.p. 84°, *n*-amyl-, phenyl-, m.p. 126°, *o*-, m.p. 141°, *m*-, m.p. 92°, and *p*-tolyl-, m.p. 127°, *o*-, m.p. 127°, *m*-, m.p. 119°, and *p*-anisyl-, m.p. 165°, *o*-, m.p. 105°, *m*-, m.p. 126°, and *p*-phenetyl-, m.p. 165°, *isopropyl*-, phenyl-, m.p. 100°, *m*-, m.p. 91°, and *p*-tolyl-, m.p. 94°, *o*-, m.p. 88°, *m*-, m.p. 100°, and *p*-anisyl-, m.p. 142°, *m*-, m.p. 76°, and *p*-phenetyl-, m.p. 122°, *isobutyl*-, phenyl-, m.p. 68°, *m*-tolyl-, m.p. 71°, *o*-, m.p. 104°, and *p*-anisyl-, m.p. 126°, and *p*-phenetyl-, m.p. 102°, *isoamyl*-. The following amines are new: *isopropyl*-*o*-, b.p. 108—116° (23 mm.), *m*-, b.p. 100—104° (11 mm.), *isobutyl*-*m*-, b.p. 97—100° (1 mm.), and *isoamyl*-*m*-*toluidine*, b.p. 108—110 (1 mm.), *isopropyl*-*o*-, b.p. 111—115° (10 mm.), *m*-, b.p. 130—132° (12 mm.), *p*-, b.p. 125—129° (10 mm.), *isobutyl*-*o*-, b.p. 108—114° (4 mm.), *m*-, b.p. 148—153° (10 mm.), *p*-, b.p. 138—152° (10 mm.), *isoamyl*-*o*-, b.p. 118—124° (1.2 mm.), and *p*-*anisidine*, b.p. 137—141° (1.2 mm.), *isopropyl*-*o*-, b.p. 119—122° (12 mm.), *m*-, b.p. 137—143° (14 mm.), *p*-, b.p. 138—142° (13 mm.), *isobutyl*-*m*-, b.p. 135—139° (1.6 mm.), *p*-, b.p. 135—149° (4 mm.), and *isoamyl*-*p*-*phenetidine*, b.p. 154—164° (4 mm.). With homologous carbamides the min. hypnotic dose and min. lethal dose vary inversely with m.p. and H₂O solubility, and directly with mol. wt., heptane : H₂O distribution coeff., and power for lowering γ of H₂O. The *iso*-compounds are generally less active physiologically than the *n*-alkyl isomerides. The anisyl compounds are the least active. J. N. A.

Co-ordination compounds of semicarbazide, phenylsemicarbazide, *m*-tolylsemicarbazide, and aminoguanidine. G. S. SMITH (J.C.S., 1937, 1354—1358).—Semicarbazide or its hydrochloride in H₂O with the appropriate metal salt yields the following co-ordination compounds; *disemicarbazido*-Fe^{II} sulphate, *-Zn* sulphate, *-Co* sulphate, *-Co* chloride, *-Ni* chloride, *-Ni* sulphate, and *-Ni* oxide; *semicarbazido*-Cd chloride; *trisemicarbazido*-Ni chloride trihydrate, *-Ni* sulphate, *-Ni* nitrate, and *-Co* nitrate. With 4-phenylsemicarbazide the following are formed: *di*-4-phenylsemicarbazido-Fe^{II} sulphate, *-Cd* chloride, and *tri*-4-phenylsemicarbazido Ni chloride, *-Ni* sulphate, *-Co* chloride; with 4-*m*-tolylsemicarbazide, *di*-4-*m*-tolylsemicarbazido-Cd chloride and *tri*-4-*m*-tolylsemicarbazido-Ni nitrate are obtained, and from aminoguanidine, *diaminoguanidino*-Ni nitrate and chloride. J. D. R.

Addition of thiocyanic acid to olefinic double bonds. M. S. KHARASCH, E. M. MAY, and F. R. MAYO (J. Amer. Chem. Soc., 1937, 59, 1580).—HCNS

adds to CMe₂:CH₂, CMe₂:CHMe, CHPh:CH₂, Δ^{β} -pentene, and camphene. CMe₂:CH₂ gives 32% of BuⁿCNS and 62% of BuⁿSCN. The prep. of BuⁿCNS (42% pure), b.p. 53—54°/25 mm., is modified.

R. S. C.

Simple compounds of cyanogen. IV. Dibromomalononitrile and its conversion into sodioazidomalononitrile and a bimolecular cyanoazide, C₂N₈. E. OTT and H. WEISSENBURGER (Ber., 1937, 70, [B], 1829—1834).—CBr₂(CN)₂, obtained by bromination of CH₂(CN)₂ in H₂O, sometimes decomposes spontaneously into CHBr₂.CO₂H when its solution in Et₂O is dried; this can be avoided by addition of CCl₄. The compound from KI and CBr₂(CN)₂ regarded previously (A., 1922, i, 643) as Cl₂(CN)₂ is an additive compound, [CBr₂(CN)₂]₄.KI; the substances [CBr₂(CN)₂]₄.NaI, [CBr₂(CN)₂]₄.NaClO₃, [CBr₂(CN)₂]₄.NaCl, [CBr₂(CN)₂]₄.NaBr, and [CBr₂(CN)₂]₄.KBr are obtained analogously. These can be washed thoroughly with cold H₂O without loss of alkali salt but are decomposed by warm H₂O with separation of CBr₂(CN)₂ which is thus readily purified. NaN₃ and CBr₂(CN)₂ in H₂O-Et₂O at 0° give the very unstable bimol. cyanazide (I), C₂N₈, decomp. 127°, explosion temp. 143—144°. The *Ag* compound of (I) differs from the similarly obtained substance from the azide, m.p. 40.5°. Treatment of NaN₃ with CBr₂(CN)₂ (3 : 1) and evaporation of the solution at 35°/vac. gives the *Na* derivative of azidomalononitrile which explodes at 179—180° when rapidly heated and affords (I) when treated with acid. Sodioazidocyanoacetamide (corresponding *Ag* and *Cu* salts) is described. H. W.

Ultra-violet isomerisation of fumaronitrile. J. JENNEN (Bull. Soc. chim. Belg., 1937, 46, 258—261).—Irradiation of fumaronitrile in COMe₂ with ultra-violet light for about 100 hr. (temp. 40—50°) gives maleonitrile and an additive compound, m.p. 40—40.4°, considered to be CN·CH·C(CN)·CMe₂·OH. It is hydrolysed by conc. HCl to hydroxyisoterebic acid (Fittig, A., 1904, i, 418). H. G. M.

Itacononitrile. J. DE WOLF (Bull. Soc. chim. Belg., 1937, 46, 256—257).—Attempts to prepare itacononitrile by heating the amide with P₂O₅, and alone, failed, a small amount of *itaconimide*, m.p. 103.2—103.6°, being produced. H. G. M.

Relative and absolute spatial configurations of optically active tri-diamine complexes of chromium, cobalt, and rhodium.—See A., I, 445.

Transformations of cyclopentadiene. J. VON BRAUN, E. KAMP, and J. KOPP (Ber., 1937, 70, [B], 1750—1760).—*cyclopentenyl* chloride (I) and MgEtBr give Δ^2 -ethylcyclopentene (II), b.p. 99—103°/758 mm., in 30% yield. The corresponding dibromide, b.p. 98—100°/12 mm., like its homologues, does not readily lose HBr under the action of *tert.* bases. (II) and fuming HBr afford 3-bromoethylcyclopentane, b.p. 84—86°/42 mm., which with Mg and CO₂ gives 3 : 3'-diethyldicyclopentyl, b.p. 125°/15 mm., and ethylcyclopentane-3-carboxylic acid (III), b.p. 132—134°/15 mm. PCl₅ transforms (III) into the chloride, b.p. 76—78°/11 mm., converted by Br at 125° into 3-bromo-1-ethylcyclopentane-3-carboxyl chloride, b.p.

110°/11 mm.; this is transformed by NaN_3 followed by EtOH and KOH and then by HCl into 1-ethylcyclopentan-3-one, b.p. 150° (semicarbazone, m.p. 175°; product $\text{C}_{20}\text{H}_{18}\text{O}_5\text{N}_2$, m.p. 142°, with $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$). Δ^2 -isocyclopentene, b.p. 86–87°/59 mm., is converted into 3-bromoisoamylcyclopentane, b.p. 109–110°/15 mm., and thence into diisocamylidicyclopentyl, b.p. about 190°/19 mm., and isoamylcyclopentane-3-carboxylic acid, b.p. 160°/20 mm. (I) and Mg dodecyl chloride afford Δ^2 -n-dodecylcyclopentene (IV), b.p. 172°/15 mm., whence 3-bromo-n-dodecylcyclopentane, b.p. 163°/0.1 mm. This with Mg followed by CO_2 yields n-dodecylcyclopentane-3-carboxylic acid, m.p. 29°, n-dodecylcyclopentane, b.p. 175°/15 mm., also obtained by hydrogenation (Pd) of (IV), and 3:3'-didodecylidicyclopentyl, b.p. about 260°/0.2 mm. (IV) gives a dibromide, b.p. about 180°/0.2 mm. Δ^2 -cyclopentenylcyclopentane, b.p. 63°/9 mm., from (I) and Mg cyclopentyl bromide in 60% yield, affords 3-bromodicyclopentyl, b.p. 115°/9 mm., which gives dicyclopentyl, b.p. 67°/9 mm., tetracyclopentyl, b.p. 205–207°/9 mm., and cyclopentylcyclopentane-3-carboxylic acid, b.p. 172°/13 mm. The corresponding acid chloride, b.p. 125°/10 mm., is transformed into the Br-derivative, b.p. 128–132°/0.3 mm., which affords 1-cyclopentylcyclopentan-3-one [oxime, b.p. 145–146°/10 mm., m.p. 46° (1-cyclopentylcyclopentan-2-oneoxime, m.p. 78–79°); semicarbazone, m.p. 184°; derivative $\text{C}_{24}\text{H}_{22}\text{O}_5\text{N}_2$, m.p. 172°, with $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$]. Δ^2 -cyclohexenylcyclohexane, b.p. 80–85°/12 mm., is converted by fuming HBr at 100° into 3-bromo-1-cyclohexylcyclopentane, b.p. 132–136°/11 mm., which gives cyclopentylcyclohexane, b.p. 86–88°/11 mm., 3:3'-dicyclohexylidicyclopentyl, b.p. about 180°/0.1 mm., and 1-cyclohexylcyclopentane-3-carboxylic acid, b.p. 180°/11 mm. The acid chloride, b.p. 142–144°/11 mm., is transformed into the α -bromo-derivative, b.p. 140–142°/0.05 mm., whence cyclohexylcyclopentan-3-one (semicarbazone, m.p. 186°; compound $\text{C}_{25}\text{H}_{24}\text{O}_5\text{N}_2$, m.p. 122°, with $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$). *Et* Δ^2 -cyclopentenylacetate, b.p. 81°/12 mm., best obtained from the acid, EtOH , and H_2SO_4 , is reduced by Na and EtOH to β - Δ^2 -cyclopentenylethyl alcohol (V), b.p. 82–83°/15 mm., readily hydrogenated (Pd) to β -cyclopentenylethyl alcohol, b.p. 84–85°/11 mm., also obtained by reduction of *Et* cyclopentylacetate and smoothly transformed by HBr at 100° into β -cyclopentenylethyl bromide, b.p. 70–71°/11 mm. (V) and fuming HBr at $>70^\circ$ give a mixture (VI) of unchanged alcohol and the corresponding unsaturated bromide and β -3-bromocyclopentenylethyl bromide (VII), b.p. 100°/0.4 mm. (VI) and NHMe_2 in C_6H_6 at 100° give dimethyl- β -cyclopentenylethylamine, b.p. 66–68°/13 mm. (picrate, m.p. 136–138°; platinichloride, m.p. 148°; methiodide, m.p. 223°). (VII) is converted by Na in Et_2O containing a little EtOAc into a mixture of hydrocarbons $(\text{C}_7\text{H}_{12})_n$. When treated with Mg followed by CO_2 (VII) gives a mixture of acids. $\text{CHNa}(\text{CO}_2\text{Et})_2$ and (VII) in EtOH afford *Et*₂ dicyclo-(1:2:3)-octanedicarboxylate, b.p. 155–160°/12 mm., hydrolysed by conc. KOH to the corresponding dicarboxylic acid, m.p. 189–190° (decomp.), which, when distilled, gives dicyclo-[1:2:3]-octanecarboxylic acid, b.p. 150–152°/13 mm. H. W.

[Biological] dehydrogenation of the cyclohexane ring.—See A., III, 384.

Oxidation of cyclohexene and Δ^2 - and Δ^3 -nonenes with selenium dioxide. A. GUILLEMONAT (Compt. rend., 1937, 205, 67–68).—Oxidation (cf. A., 1936, 51) of cyclohexene affords only Δ^1 -cyclohexen-3-ol, whereas oxidation of Δ^2 - or Δ^3 -nonene leads to a mixture of alcohols as each C next to the double linking is oxidised. J. L. D.

Isomerisation of carotenes by chromatographic adsorption. II. Neo- α -carotene. A. E. GILLAM, M. S. EL RIDI, and S. K. KON (Biochem. J., 1937, 31, 1605–1610).—A new pigment, neo-carotene (I), is produced by repeated adsorption of α -carotene (II) on Al_2O_3 . The absorption max. are at 501 and 470 m μ . in CS_2 , compared with 508 and 477 for (II). On crystallisation neo- α -carotene (III), m.p. 172°, $[\alpha]_{\text{D}}^{20} +220^\circ$ in C_6H_6 , is obtained. Biologically (III) has 0.7 of the potency of β -carotene (IV), ψ - α -carotene is at least as potent as (IV), and (I) has $>1/10$ the potency of (IV). (III) is probably a geometrical isomeride of (II). P. G. M.

Condensation of alcohols with benzene in presence of aluminium chloride. S. ISHIKAWA and G. MAEDA (Sci. Rep. Tokyo Bunrika Daigaku, 1937, 3, A, 157–164).— $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$, C_6H_6 , and AlCl_3 at 100° but not at 50–60° give dibenzyl (I) in 39.8% yield; dilution of the mixture with CS_2 diminishes the yield. It appears probable that $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$ is first formed and in part condenses with C_6H_6 to (I) and in part yields styrene which passes into resinous matter. *l*-Menthyl, C_6H_6 , and AlCl_3 afford *p*-menthene, b.p. 166–167°, and 3-phenylmenthane, b.p. 275°/760 mm., $[\alpha]_{\text{D}}^{25} -3.898^\circ$ in C_6H_6 , which does not decolorise Br in CHCl_3 and is converted by fuming HNO_3 into a resin and thence into $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. cycloHexanol, C_6H_6 , and AlCl_3 yield cyclohexene, phenylcyclohexane, b.p. 238°/761 mm., oxidised to $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and small amounts of 1:2-diphenylcyclohexane, m.p. 173° (corr.; Berl). Definite products could not be obtained by condensation of $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ or $(\text{CH}_2\cdot\text{OH})_2$ with C_6H_6 and AlCl_3 . H. W.

Dealkylation of dialkylbenzenes. V. N. IPATIEV and B. B. CORSON (J. Amer. Chem. Soc., 1937, 59, 1417–1418).— FeCl_3 in C_6H_6 at 83° dealkylates *ditert.*-alkylbenzenes, but not the primary or *sec.* alkyl compounds. This is proved for *p*-*ditert.*-butyl- (I) and -amyl-benzene, $p\text{-C}_6\text{H}_4\text{Pr}^t_2$, $\text{-C}_6\text{H}_4(\text{CHMeEt})_2$ (II), $\text{-C}_6\text{H}_4\text{MePr}^t$, and $\text{-C}_6\text{H}_4\text{Et}_2$. A mixture of (I) and (II) yields PhBu^t and unchanged (II). (I) and H_2SO_4 in C_6H_6 at 15° give PhBu^t and $p\text{-C}_6\text{H}_4\text{Bu}^t\cdot\text{SO}_3\text{H}$, formation of the acid indicating that dealkylation precedes substitution. (I) and H_3PO_4 in C_6H_6 at 90°, 150°, 200°, 250°, and 300° give 0, 0, 2, 19, and 23%, respectively, of PhBu^t . 71% HClO_4 in C_6H_6 at 85° is without effect on (I). R. S. C.

Reactions in the presence of metallic halides. II. Behaviour of fluorides and the reactivity of the halogens. N. O. CALLOWAY (J. Amer. Chem. Soc., 1937, 59, 1474–1479; cf. this vol., 293).— C_6H_6 , AcF , and AlCl_3 give 41.6% of COPhMe , and Bu^tF gives PhBu^t . ZnF_2 gives 1.3% of

$p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ from AcCl and PhOMe , and 30.6% of $p\text{-C}_6\text{H}_4\text{Bu}\cdot\text{OMe}$ from BuCl and PhOMe , but only 0.06% of 2-acetylfuran with much tar from furan and AcCl . In all cases both HCl and HF are evolved, owing to reaction between the HHal and the halide. AlF_3 does not cause reaction of C_6H_6 with AcF or Bu^+F , or of PhOMe with AcCl . ZnF_2 does not cause reaction of PhOMe with AcF , Bu^+Cl , or Bu^+Br , or of furan with AcCl . Bu^+I , C_6H_6 , and AlCl_3 at 29° give no HHal . As judged by the temp. at which evolution of HHal is approx. the same, the order of activity for acyl halides is $\text{I} > \text{Br} > \text{Cl} > \text{F}$, but for alkyl halides $\text{F} > \text{Cl} > \text{Br} > \text{I}$. The validity of this method of assessment is discussed and upheld. The change, the ease of which is measured, is probably $\text{RX}\cdot\text{AlCl}_3\cdot\text{C}_6\text{H}_6 \rightarrow \text{RPh}\cdot\text{AlCl}_3\cdot\text{HX}$. R. S. C.

Diazonium borofluorides. II. Their use in the preparation of nitro-compounds. E. B. STARKEY (J. Amer. Chem. Soc., 1937, 59, 1479—1480; cf. this vol., 39).—Difficultly accessible aromatic NO_2 -compounds are obtained by treating the diazonium borofluorides with Cu and aq. NaNO_2 at room temp. The following yields were obtained: PhNO_2 20, o -33, m -43, and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ 64, o -32, and $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ 15, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ 10, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ 50, and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NPh}$, $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{NO}_2$, and $1\text{-C}_{10}\text{H}_7\cdot\text{NO}_2 < 10\%$. R. S. C.

Preparation of *m*-dinitrobenzene. S. V. SHAH (J. Chem. Educ., 1937, 14, 322).—A correction (cf. this vol., 182). L. S. T.

Radicals with several tervalent carbon atoms. M. LEO (Ber., 1937, 70, [B], 1691—1694).— Me_3 trimesate is converted by LiPh in Et_2O into $1:3:5\text{-trihydroxybenzhydrylbenzene}$, m.p. 188—189°, transformed by AcCl into $1:3:5\text{-trichlorobenzhydrylbenzene}$, m.p. 203—204°; 2% solutions of this in C_6H_6 are colourless and are dehalogenated by Cu powder to solutions which do not show a dark, characteristic colour coupled with the development of absorption bands. Only partial decolorisation occurs when the solution is shaken with air. The free radical (I) is freely sol. in most media but appears mainly unimol. in solution. It appears therefore that the free valencies saturate one another within the mol., at any rate in some degree. $2:7\text{-C}_{10}\text{H}_6\text{Bz}_2$ and LiPh afford $2:7\text{-dihydroxybenzhydrylnaphthalene}$, m.p. 141—145°, converted into $2:7\text{-dichlorobenzhydrylnaphthalene}$, m.p. 176—178°, dehalogenated solutions of which behave like those of (I). H. W.

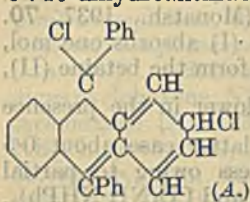
Dehydrogenation. I. Catalytic dehydrogenation of hydronaphthalenes with and without an angular methyl group. R. P. LINSTEAD, A. F. MILLIDGE, S. L. S. THOMAS, and A. L. WALPOLE (J.C.S., 1937, 1146—1157).—1-Ketodecahydronaphthalene with MgMeI yields 1-hydroxy-1-methyl-decahydronaphthalene, b.p. 112—113°/10 mm., dehydrated ($\text{H}_2\text{C}_2\text{O}_4$) to 1-methyl-3:4:5:6:7:8:9:10-octahydronaphthalene, b.p. 81—83°/10 mm., reduced (Pt-H_2) to 1-methyldecahydronaphthalene, b.p. 80—81°/12 mm. *trans*-2-Methyloctahydronaphthalene affords a nitroschloride, m.p. 138°. In the liquid phase at the b.p. of the hydrocarbon, tetra- and deca-

hydronaphthalene with Pt -asbestos or 30% Pd-C yield C_{10}H_8 whilst octahydronaphthalene with 25% Pd-C gives a mixture of C_{10}H_8 and tetra-, octa-, and deca-hydronaphthalene. 1- and 2-Methyloctahydronaphthalene yield with Pd-C , 1- and 2- $\text{C}_{10}\text{H}_7\text{Me}$, respectively, the latter also affording some *trans*-2-methyldecahydronaphthalene; 9-methyloctahydronaphthalene is unchanged, and 1:10-dimethyl-octahydronaphthalene affords 1:5- $\text{C}_{10}\text{H}_6\text{Me}_2$. In the vapour phase *cis*-decahydronaphthalene over Pt or Pd yields C_{10}H_8 ; 1-methylocta- and 1-methyldecahydronaphthalene give 1- $\text{C}_{10}\text{H}_7\text{Me}$, and 9-methyl-deca- or -octa-hydronaphthalenes over Pt-C affords chiefly C_{10}H_8 and a trace of 1- $\text{C}_{10}\text{H}_7\text{Me}$, over 30% Pd-C a mixture of C_{10}H_8 and 1- $\text{C}_{10}\text{H}_7\text{Me}$, and over Pt -asbestos chiefly 1- $\text{C}_{10}\text{H}_7\text{Me}$. 4:9-Dimethyl-octahydronaphthalene over Pt -asbestos yields 1:5- $\text{C}_{10}\text{H}_6\text{Me}_2$ and a dimethylnaphthalene (I) (*picrate*, m.p. 134—134.5°; *styphnate*, m.p. 145°), whilst over 30% Pd-C , 1- $\text{C}_{10}\text{H}_7\text{Me}$ is formed; from 4:9-dimethyldecahydronaphthalene with 30% Pd-C , 1- $\text{C}_{10}\text{H}_7\text{Me}$ and 1:5- $\text{C}_{10}\text{H}_6\text{Me}_2$ are formed. Methyl-octahydronaphthalene (II), made by the dehydration of 1-methyl-2-butenylcyclohexanol, with 30% Pd-C affords C_{10}H_8 and 1- $\text{C}_{10}\text{H}_7\text{Me}$ and with Pt -asbestos, only 1- $\text{C}_{10}\text{H}_7\text{Me}$, proving (II) to be essentially the 9-Me compound, whilst the methyloctahydronaphthalene from 2-methyl-1-butenylcyclohexanol with 30% Pd-C gave C_{10}H_8 and a trace of 1- $\text{C}_{10}\text{H}_7\text{Me}$, and with Pt -asbestos, only 1- $\text{C}_{10}\text{H}_7\text{Me}$, showing it to be a mixture of the 1- and 9-Me compounds. γ -o-Tolyl-valeryl chloride with CS_2 and AlCl_3 affords 1-*keto*-4:5-dimethyltetrahydronaphthalene, b.p. 154—156°/18 mm., m.p. 56°, reduced (Na-EtOH) to the corresponding alcohol, which is dehydrogenated (Se) to 1:8-dimethylnaphthalene, b.p. 140/18 mm., m.p. 63°. (I) is not identical with 1:2-, 1:4-, 1:5-, or 1:8- $\text{C}_{10}\text{H}_6\text{Me}_2$. J. D. R.

Structure of naphthalene, hydrindene, and tetralin derivatives. (MISS) N. McLEISH and N. CAMPBELL (J.C.S., 1937, 1103—1108).—Existing evidence in favour of a static 1:2 ethylenic linking in C_{10}H_8 is reviewed and supported by the facts that the Br in 1:2-, 2:1-, and 4:1- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NO}_2$ is reactive towards piperidine, and non-reactive in other bromonitronaphthalenes; the same applies to the chloronitronaphthalenes. Similarly the reactivity of the Br in 6-bromo- and non-reactivity in 4-bromo-5-nitrohydrindene confirms the structure of hydrindene, but although the Br in 6-bromo-7-nitro- is reactive, and in 6-bromo-5-nitro-tetrahydronaphthalene is unreactive, the evidence is too conflicting to decide the positions of the double linkings. 6:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}_2$, by diazotisation and treatment with $\text{CuSO}_4\text{-SO}_2$, affords 6-bromo-2-nitronaphthalene, m.p. 190°. 6-Bromo-5-aminohydrindene in $\text{C}_5\text{H}_5\text{N}$ with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and Br affords 4:6-dibromo-5-p-toluenesulphonamidohydrindene, m.p. 199—200°, hydrolysed (H_2SO_4) to 4:6-dibromo-5-aminohydrindene, m.p. 71° (lit. 70°), reduced by Sn-HCl-EtOH to 4-bromo-5-aminohydrindene, m.p. 50—51°, converted by diazotisation and $\text{CuSO}_4\text{-SO}_2$ into 4-bromo-5-nitrohydrindene (an oil). 6-Bromo-5-aminohydrindene was similarly converted into 6-bromo-5-nitrohydrind-

ene, m.p. 44—45°. 6-Bromo-7-, m.p. 53—54°, and 6-bromo-5-nitro-1:2:3:4-tetrahydronaphthalene, m.p. 101—102°, are formed by the usual methods from the 6-NHAc-compounds. J. D. R.

Tautomerisation reactions in the anthracene series. E. BERGMANN and O. BLUM-BERGMANN (J. Amer. Chem. Soc., 1937, 59, 1439—1441).—9:10-Dichloro-9:10-diphenyl-9:10-dihydroanthracene in boiling AcCl gives HCl and 2-chloro-9:10-dihydroanthracene, synthesised by treating

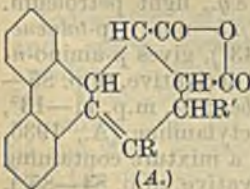


1-chloroanthraquinone with MgPhBr and dehydrating the product by boiling HCO₂H. The decomp. is assumed to involve formation of the quinolid product (A) and thence of 2:9-dichloro-9:10-diphenyl-9:10-dihydroanthracene.

The 9:10-dichloro-9:10-diphenyl compound is so unstable that HCl in boiling C₆H₆ converts 9:10-dihydroxy-9:10-di- α -naphthyl-9:10-dihydroanthracene directly into 2-chloro-9:10-di- α -naphthylanthracene (synthesised from the chloroquinone and 1-C₁₀H₇-MgBr). Several known reactions, which are best explained by quinolid tautomerisation, are discussed. R. S. C.

Synthesis of triphenylene. E. BERGMANN and O. BLUM-BERGMANN (J. Amer. Chem. Soc., 1937, 59, 1441—1442).—Mg 9-phenanthryl bromide and (-CH₂CO)₂O in Et₂O give γ -keto- γ -9-phenanthrylbutyric acid, m.p. 176° (Me ester, m.p. 88°), the semicarbazone, m.p. 237° (decomp.), of which with NaOEt in H₂ at 200° gives γ -9-phenanthrylbutyric acid, m.p. 173°; this is cyclised by P₂O₅ in PhMe at 100° to 4-keto-1:2:3:4-tetrahydrotriphenylene, m.p. 101°, which affords (Clemmensen) 1:2:3:4-tetrahydrotriphenylene, m.p. 120—121° (obtained in small yield by dehydrogenation of dodecahydrotriphenylene), and a little (?) di-1:2:3:4-tetrahydro-4-triphenylenyl, m.p. 300°. The former hydrocarbon and Se at 320° give triphenylene (9:10-benzphenanthrene). R. S. C.

Diene reactions involving aromatic nuclei. Phenanthrene system. E. BERGMANN and F. BERGMANN (J. Amer. Chem. Soc., 1937, 59, 1443—1450).—Maleic anhydride (I) adds to 9-vinylphenanthrene and to some, but not to all, α - and β -substituted derivatives thereof, occurrence or absence of addition depending on both the nature and position of the substituent. The greater reactivity of the phenanthrene as compared with the C₁₀H₈ derivatives is ascribed to the more olefinic nature of the phenanthryl radical. Phenanthrene derivatives which form adducts give orange-red or red picrates; similar saturated or unreactive derivatives form yellow picrates. The reactions described below are for synthesis or proof of structure. The following are prepared by the Grignard reaction, the adducts mentioned being of type (A), no addition occurring if no adduct is mentioned: 1-cyclopentenyl-, b.p. 115°/0.04 mm. (picrate, m.p. 82°), and



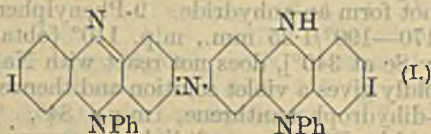
6-methoxy-1-cyclopentenyl-naphthalene, m.p. 148°, 9-allyl- (II), b.p. 161—163°/1.25 mm. (picrate, m.p. 115°), 9-isopropenyl-, m.p. 38°, b.p. 163°/20 mm. (purified by H₂C₂O₄ at 150°; picrate, m.p. 108°; adduct, m.p. 262°), 9-1'- Δ^1 -cyclopentenyl-, b.p. 185°/0.85 mm. [purified by H₂C₂O₄; some 9:9-diphenanthryl (III), b.p. 220—250°/3 mm. (picrate, m.p. 163°), also formed; picrate, m.p. 120°; adduct (IV), m.p. 275—276°], and 9-1'- Δ^1 -cyclohexenyl-phenanthrene (V), m.p. 132°, b.p. 190—200°/1.25 mm. (picrate, m.p. 141—142°), benzyl-9-phenanthrylcarbinol (VI), m.p. 120°, the acetate of which at the b.p., 220—240°/0.4 mm., gives 9-styrylphenanthrene (VII), m.p. 118° (dipicrate, m.p. 164°, unstable; adduct, m.p. 249—250°), α -9-phenanthrylstyrene (VIII), b.p. 180—190°/1 mm., m.p. 142°, 3-9'-phenanthrylindene, b.p. 230°/0.7 mm., m.p. 121.5° (picrate, m.p. 132°), and 4-9'-phenanthryl-1:2-dihydronaphthalene, b.p. 220—300°/1.25 mm., m.p. 184.5°. The reversible nature of the diene reaction is proved by the observation that formation of (IV), which is completely insol. in the solvent, ceases short of completion, but can be thereafter continued if the adduct formed is removed and heating of the mother-liquor is continued. 1-Vinylnaphthalene and (I) in boiling xylene give tetrahydrophenanthrene-1:2-dicarboxylic anhydride, m.p. 169—170°, and acid, m.p. 244° (decomp.). α -9-Phenanthrylethyl alcohol with Ac₂O gives the acetate, m.p. 107°, and with KHSO₄ affords a polymeride (? dimeride), b.p. 280°/0.2 mm. (picrate, m.p. 173°), of 9-vinylphenanthrene, the monomeric form of which was once obtained, b.p. 150—160°/1 mm. [with (I) gives tetrahydrotriphenylene-1:2-dicarboxylic acid, m.p. 218—220°, autoxidisable, from the Me xanthogenate; this derivative, however, usually gave 9-ethylphenanthrene. The Tschugaev reaction with (VI) leads to a similar reduced product, 9- β -phenylethylphenanthrene (IX), b.p. 220—230°/0.8 mm., m.p. 81.5° (picrate, m.p. 133°). KOH-EtOH isomerises (II) to 9-propenylphenanthrene, b.p. 179°/2.5 mm. (picrate, m.p. 108°), which with (I) gives the adduct, m.p. 264°. The structure of (V), which is unchanged by AlCl₃, is proved by reaction with Br, formation of a violet colour with hot conc. H₂SO₄, and oxidation (CrO₃) to phenanthrenequinone; its failure to react with (I) is ascribed to fixation of the 9:10- and Δ^1 -ethylenic linkings in the *trans*-position to each other. By reaction with Na (VIII) affords $\alpha\delta$ -diphenyl- $\alpha\delta$ -di-9-phenanthrylbutane, m.p. 243.5°, and (III) gives 10:10'-dihydro-9:9'-diphenanthrylidene, m.p. 303° [perbromide (Br₂), cryst.]. A Na₂ derivative is obtained from (VII) and thence by isomerisation in alkali (IX); that isomerisation occurs at this stage is evidenced by the fact that the Na₂ salt and dry CO₂ give a dicarboxylic acid, m.p. 279°, which does not form an anhydride. 9-Phenylphenanthrene, b.p. 170—190°/1.25 mm., m.p. 110° [obtained from (V) by Se at 340°], does not react with Na, but with Li rapidly gives a violet solution and thence 9-phenyl-9:10-dihydrophenanthrene, m.p. 84°, previously obtained by PCl₅ from α -2-diphenylstyrene, the latter reaction being thus proved to have involved ring-closure. CH₃CNa and cyclohexanone give 2-hydroxycyclohexylacetylene (X), b.p. 86°/17 mm., and the glycol, b.p. 160—164°/3 mm., m.p. 102—103°.

Hydrogenation of (X) under all conditions tried gives mainly ethylcyclohexanol, b.p. 70–75°/18 mm., but the crude product contained some 1-vinylcyclohexan-1-ol, since dehydration with $\text{H}_2\text{C}_2\text{O}_4$ gives polymeric 1-vinyl- Δ^1 -cyclohexene, b.p. 160°, as well as ethylcyclohexene, b.p. 49°/30 mm. With $\text{H}_2\text{C}_2\text{O}_4$ at 150° (30 min.) (X) gives cyclohexanone and, by rearrangement to cyclohexenylacetaldehyde, followed by oxidation, also some cyclohexenylacetic acid. $\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and CH_3CNa give γ -hydroxy- γ -phenyl- Δ^1 -n-hexenoic acid, m.p. 242.5°, and, by condensation of 2 mols. of the ester, 2:5-dibenzoylcyclohexane-1:4-dione, m.p. 200° (bisphenylhydrazone, m.p. 274°; Me_2 ether, m.p. 204°), which probably exists as the dienol since it dissolves in alkali to give dark solutions. R. S. C.

Tar hydrocarbons. I. Reduction products of pyrene. E. A. COULSON (J.C.S., 1937, 1298–1305).—Pyrene (I) hydrogenated (H_2 — MoO_3 — S-C) at 400°/100 atm. in 4 hr. yields 3:4:5:8:9:10: (II) and 1:2:3:4:5:12-hexahdropyrene (III), and 1:2-dihdropyrene (IV), m.p. 132° (picrate, m.p. 147°); in 6 hr., 1:2:6:7-tetrahydropyrene (V), m.p. 138°, is also formed. With Na in boiling $\text{C}_5\text{H}_{11}\text{-OH}$, (I) yields (II) and (III), and some decahydropyrene; (III) yields (IV), (IV) yields 1:2:3:4:5:6:7:12:13:16-decahydropyrene (VI), m.p. 68°, (II) yields 1:2:3:4:5:8:9:10:11:12-decahydropyrene (VII), m.p. 68°, whilst (III) gives a mixture of (VI) and (VII). (IV) when oxidised (H_2O_2 in AcOH) gives 9:10-dihydrophenanthrene-4:5-dicarboxylic acid, m.p. 256°, and with aq. KMnO_4 , diphenyl-2:6:2':6'-tetracarboxylic acid (VIII), also obtained by oxidation (aq. KMnO_4) of (V). 2-Bromo-m-xylene, oxidised (KMnO_4) and esterified, affords *Me* 2-bromoisophthalate, b.p. 190–191°/22 mm., hydrolysed (HCl) to 2-bromoisophthalic acid, m.p. 218°, converted by Cu at 180° into (VIII). J. D. R.

Decomposition of aniline nitrite. J. C. EARL (J.C.S., 1937, 1129–1131).— NH_2Ph nitrite (A., 1933, 498) (of which the Et_2O solution is now evaporated under reduced pressure of dry N_2) decomposes in N_2 at –6° to –8°/60 mm., giving diazoaminobenzene, and a CHCl_3 -insol. liquid consisting mainly of benzene-diazonium nitrite. E. W. W.

Reaction between aniline and iodine. H. H. HODGSON and E. MARSDEN (J.S.C., 1937, 1365–1366).—At 20–150° I iodates NH_2Ph , the products being $p\text{-C}_6\text{H}_4\text{I}\cdot\text{NH}_2$ and $\text{NH}_2\text{Ph}\cdot\text{HI}$ if 1 mol. of I is used, but including 2:4- $\text{C}_6\text{H}_3\text{I}_2\cdot\text{NH}_2$ if >1 mol. of I is used. At >150° a vat dye, $\text{C}_{36}\text{H}_{23}\text{N}_5\text{I}_2$, probably (I), is formed, which is also obtained from $p\text{-C}_6\text{H}_4\text{I}\cdot\text{NH}_2$ and



NH_2Ph at 220–230°. Pure $p\text{-C}_6\text{H}_4\text{I}\cdot\text{NH}_2$ at 220° gives only 2:4- $\text{C}_6\text{H}_3\text{I}_2\cdot\text{NH}_2$ and I. Distillation of (I) with Zn dust gives NH_3 , PhNC , NH_2Ph , and phenazine. R. S. C.

Diphenylcarbazone. P. KRUMHOLZ and E. KRUMHOLZ (Monatsh., 1937, 70, 431–436).—The material, m.p. 157°, previously considered to be diphenylcarbazone (I), $\text{NPh}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{NPh}$, is a 1:1 mol. compound thereof with $\text{CO}(\text{NH}\cdot\text{NPh})_2$, from which it is separated by its solubility in alkali. Pure (I) (*Na* salt) has m.p. 127° and k_s about 10^{-8} , and gives the reactions previously held to be characteristic of (I), except the CrO_4^{2-} reaction. R. S. C.

Auto-oxidation of diphenylcarbazone. P. KRUMHOLZ and H. WATZKE (Monatsh., 1937, 70, 437–446).—Diphenylcarbazone (I) absorbs one mol. of O_2 in the presence of NH_3 to form the betaine (II), $\text{NPh}\cdot\text{N}^-\text{C}\cdot\text{O}^-$. Oxidation is slower in the presence of Na_2CO_3 or NH_4Cl ; in the latter case about 0.5 mol. of O_2 is utilised, doubtless owing to partial disproportionation of (I) to (II) and $\text{CO}(\text{NH}\cdot\text{NPh})_2$. In the absence of O_2 1 mol. of (I) is oxidised by $2\text{CuO}\cdot\text{NH}_3$; even traces of Cu catalyse the aerial oxidation enormously and the oxidation occurring when it is not added is believed to be due to unavoidable traces; $0.5\text{--}1 \times 10^{-7}$ mol. of Cu per litre as impurity would suffice to give the observed rate of oxidation. This hypothesis is supported by the fact that 3×10^{-7} mol. of KCN per litre prevents oxidation, presumably by formation of CuCN which cannot be oxidised by air to Cu^{II} . The rate of oxidation is independent of the (I) concn., but depends on the [Cu] and $[\text{NH}_3]$; with 3.75×10^{-7} mol. of Cu per litre, this rate is a max. in 0.1N- NH_3 . Other bases and catalytically active metals may be used, but are less effective, especially the metals. R. S. C.

Rearrangement of the alkyylanilines. VIII. Migration of large groups. W. J. HICKINBOTTOM (J.C.S., 1937, 1119–1125; cf. A., 1932, 1124).—*n*-Amylaniline heated with CoCl_2 or CoBr_2 yields *p*-amino-*n*-amylbenzene, b.p. 130°/16 mm. (hydrochloride; sulphate; Ac, m.p. 101°, and *p*-toluenesulphonyl, m.p. 68–69°, derivatives), with *amylamino*-amylbenzene (?), b.p. 180–185°/16 mm. *n*-Hexylaniline, b.p. 158°/28 mm. (hydrobromide; *p*-toluene-, m.p. 67–68°, and *m*-nitrobenzene-sulphonyl derivative, m.p. 79–80°) (from NH_2Ph and *n*- $\text{C}_6\text{H}_{13}\text{I}$), gives *p*-amino-*n*-hexylbenzene, b.p. 146–148°/17 mm. (hydrochloride; sulphate; Ac derivative, m.p. 91°, with *p*-*n*-hexylamino-*n*-hexylbenzene, b.p. 203–204°/18 mm. [hydrochloride (I)]. *n*-Heptylaniline, b.p. 160–161°/21 mm. (hydrobromide; *p*-toluene-, m.p. 76°, and *m*-nitrobenzene-sulphonyl derivative, m.p. 96°), yields *p*-amino-*n*-heptylbenzene (II), b.p. 159°/18 mm. (hydrochloride; Ac derivative, m.p. 91–92°), with *p*-*n*-heptylamino-*n*-heptylbenzene, b.p. 220–223°/18 mm. [hydrochloride (III), m.p. 83–85°], also prepared from (II) and *n*- $\text{C}_7\text{H}_{15}\text{Br}$. The hydrochlorides (I) and (III) are sol. in org. solvents, e.g., light petroleum. *n*-Octylaniline, b.p. 177–178°/25 mm. (*p*-toluenesulphonyl derivative, m.p. 42–43°), gives *p*-amino-*n*-octylbenzene (*p*-toluenesulphonyl derivative, m.p. 85–86°), with *p*-*n*-octylamino-*n*-octylbenzene, m.p. 11–13°, b.p. 232–235°/14 mm. *sec*-Octylaniline (A., 1935, 1489) gives octene, NH_2Ph , and a mixture containing aminosec-octylbenzene (Ac derivative, m.p. 84–85°), and an isomeride. Dodecylaniline, m.p. 27–28°,

b.p. 212—214°/13 mm. (*hydrochloride*, m.p. 88—91°; *p-toluenesulphonyl* derivative, m.p. 53—54°) [obtained with *didodecylaniline* (?), b.p. 280—295°/12 mm., from $C_{12}H_{25}I$ (IV) and NH_2Ph], gives *p-aminododecylbenzene* (V), m.p. 41—42° (*Ac* derivative, m.p. 101—101.5°), with *p-dodecylaminododecylbenzene*, m.p. 48—49° (*hydrochloride*, m.p. 84—85°; *nitrosoamine*, m.p. 40—41°), also obtained from (IV) and (V). *Cetyl-aniline* (*nitrosoamine*, m.p. 40—41°; *p-toluenesulphonyl* derivative, m.p. 64—65°) yields *p-aminocetylbenzene*, m.p. 51—52° (*Ac*, m.p. 102.5—103.5°, and *p-nitrobenzylidene*, m.p. 71°, derivatives), with *p-cetylaminocetylbenzene*, m.p. 62—63° (*nitrosoamine*, m.p. 55°). *cycloHexylaniline* with $CoCl_2$ at 247° gives cyclohexene, NH_2Ph , and *p*- and *o*-aminophenylcyclohexane (A., 1932, 1242). $NH_2Ph \cdot CH_2Ph$ gives NH_2Ph , *p*-aminodiphenylmethane [*p-nitrobenzylidene* derivative, m.p. 101—102°; condensation product with 1 : 2 : 4- $C_6H_3Cl(NO_2)_2$, m.p. 128—128°; *p-benzyl- $\alpha\beta$ -diphenylthiocarbamide*, m.p. 148—149°], and *o*-aminodiphenylmethane (?), with 2 : 4-*dibenzylaniline*, m.p. 49—50° (*Ac* derivative, m.p. 145—146°), and a *tert*-amine (*mercurichloride*, m.p. 190—193°).

E. W. W.

The solid carbon-oxygen complex. I. Oxidative action of graphitic oxide and active carbon plus oxygen on some aromatic amines. A. H. CARTER, L. DE V. MOULDS, and H. L. RILEY (J.C.S., 1937, 1305—1312).—The amine was heated for several hr. on the water-bath with graphitic oxide (I), the prep. of which is described. (a) Pure NH_2Ph afforded azophenine (II) and a mauveine-type dye (III). Commercial NH_2Ph containing *o*- and *p*- $C_6H_4Me \cdot NH_2$ gave (II) and (III) and a rosaniline dye (IV), (b) $NHPhMe$ yielded a complex resinous substance and $NN'N''$ -trimethylpararosanine (V), (c) $NPhMe_2$ afforded Me-violet (VI) (as sulphate), leuco-crystal-violet (VII), and 4 : 4'-dimethyldiaminodiphenylmethane (VIII). The $CHPh_3$ dyes were present as sulphates, the SO_4^{--} being derived from H_2SO_4 occluded in (I). The mechanism of the reactions is discussed, and the results show that (I) is similar in its oxidising action to PbO_2 and H_2O_2 . By bubbling air through a mixture of the amine and "active" charcoal at 100°, the following results were obtained: (a) NH_2Ph yielded tarry products and only small quantities of unidentified iminoquinone derivatives, but with H_2SO_4 -treated charcoal a little (II) and a substance probably allied to induline-3B were obtained; commercial NH_2Ph also gave (IV); (b) $NHPhMe$ gave a complex resin, but with H_2SO_4 -treated charcoal some (V) was also obtained; (c) $NPhMe_2$ gave (VII) and (VIII), but with H_2SO_4 -treated C or when H_2SO_4 was added, (VI) was also obtained. The parallelism between the results of the two methods of oxidation indicates a fundamental similarity between (I) and the active C-O complex.

J. G. A. G.

Iodination of *p*-aminobenzenesulphonamide and some symmetrical azobenzenesulphonamides. J. V. SCUDI (J. Amer. Chem. Soc., 1937, 59, 1480—1483).—*p*- $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ (I) (*Ac* derivative, m.p. 214°) and ICl in H_2O or $AcOH$ give 94 and 90%, respectively, of 3-iodo- (II), m.p. 179—180° (*Ac* derivative, m.p. 216°), and 96—99 and 73—77%, respectively, of 3 : 5-di-iodo-4-aminobenzene- Q^{**} (A., II.)

sulphonamide (III), m.p. 265° (decomp.). Hot 10% HCl and (II) give (III) and (I), and (III) and hot 20% HCl give (I) and (II). I in $NaHCO_3$ or $NaOH$ or $KMnO_4$ converts (I) into azobenzene-4 : 4'-disulphonamide, m.p. >270°. Similarly (II) gives 2 : 2'-di-iodoazobenzene-4 : 4'-disulphonamide, m.p. >270°, but (III) and $KMnO_4$ give 3 : 5-di-iodo-4-nitrosobenzenesulphonamide, m.p. >270°. R. S. C.

Preparation of [sulphonamide] compounds of therapeutic value.—See B., 1937, 842.

Associating effect of the hydrogen atom.—See A., I, 513.

Benzenesulphonyl derivatives of *o*-nitroaniline and *o*-phenylenediamine. L. H. AMUNDSEN (J. Amer. Chem. Soc., 1937, 59, 1466—1467).—Benzenesulphon-*o*-nitroanilide (I), m.p. 102.2—102.5°, is best obtained from *o*- $NO_2 \cdot C_6H_4 \cdot NH_2$ and $PhSO_2Cl$ (0.5 mol.) in dioxan. *Dibenzenesulphon-*o*-nitroanilide*, m.p. 189.8—190.5°, is best obtained from $PhSO_2Cl$ and the Na salt, m.p. 239—240°, of (I) in dioxan, and on reduction (H_2 -Pt or $Fe-AcOH$) gives *dibenzenesulphon-*o*-aminoanilide*, m.p. 149.5—149.9°. *o*- $PhSO_2 \cdot NH \cdot C_6H_4 \cdot NH_2$, m.p. 169.3—170°, gives a *benzenesulphonate*, m.p. 204.9—205.4°. *o*-($PhSO_2 \cdot NH$) $_2C_6H_4$, m.p. 190.3—190.8°, is best prepared in hot $PhMe$, and its Na_2 salt, m.p. >275°, affords *tribenzenesulphon-*o*-phenylenediamide*, m.p. 157.1—157.3°, previously held to be the $(PhSO_2)_4$ derivative. M.p. are corr. R. S. C.

Reaction of α -oxides with arylamines. J. O. GABEL (Trav. Inst. Chim. Charkov, 1935, 1, 53—67).—The author's published papers (1925—1935) are reviewed. R. T.

Stereochemistry of deuterium compounds. II. α -Methylbenzylamine. L. E. YOUNG and C. W. PORTER (J. Amer. Chem. Soc., 1937, 59, 1437—1438; cf. this vol., 132).—By several treatments with D_2O *d*- (I) (obtained as *l*-malate from the *dl*-base), $[\alpha]_{D_{40}}^{20} +44.66^\circ$, and *l*- $CHPhMe \cdot NH_2$ [obtained as *dl*-malate from the mother-liquors from (I)], $[\alpha]_{D_{40}}^{20} -45.39^\circ$, b.p. of both 187.4° (corr.), $d_{24}^{20} 0.9458$, give *d*- and *l*-*NN*-*dideutero- α -methylbenzylamine*, b.p. 188.4°, with reduced optical rotation, $[\alpha]_{D_{40}}^{20} +42.88^\circ$, -43.77°, $d_{24}^{20} 0.9615$, recovered by H_2O into $CHPhMe \cdot NH_2$ of unchanged $[\alpha]$ and *d*. R. S. C.

Stereochemistry of dicyclic ring systems. III. Stereoisomerism of hydrindane and its derivatives. IV. Hydrindanes substituted in the six-membered ring. W. HÜCKEL, R. SCHLÜTER, W. DOLL, and F. REIMER (Annalen, 1937, 530, 166—183; cf. A., 1935, 971).—The following preps. were carried out for comparative purposes to be discussed later. *cis*-Hexahydrohydrindanes substituted in the 6-membered ring behave similarly to the corresponding decahydronaphthalene derivatives. The catalytic hydrogenation of hydrindenes is much more rapid than that of the corresponding tetrahydronaphthalene derivatives. Hydrogenation of 4-acetamidoinane, m.p. 126° (100 g.), in decahydronaphthalene in the presence of Ni at 200°/80 atm. gives *forms*, m.p. 131° (55 g.) and 93° (16 g.), of 4-acetamido-*cis*-hexahydrohydrindane, a difficultly separable mixture being obtained by the use of Pt in

AcOH at 60°/4 atm.; with 20% HCl at 150—160° these give *forms*, b.p. 85°/11 mm., m.p. -14° (*Bz* derivative, m.p. 177°), and b.p. 85°/11 mm. (*Bz* derivative, m.p. 163°), of 4-amino-*cis*-hexahydrohydrindane, the former being obtained from *cis*-hydrindane-4-oxime by hydrogenation and the latter by Na-EtOH. The former base with HNO₂-AcOH gives mainly a *cis*-hexahydrohydrindan-4-ol (I), *forms*, m.p. 16° and 31°, b.p. 104°/11 mm. (*H phthalate*, m.p. 134°; *phenylurethane*, m.p. 81°; *p*-nitrobenzoate, m.p. 86°; *H succinate*, m.p. 47°), with a small amount of an oily *isomeride* (II) (*H phthalate*, m.p. 146°; *p*-nitrobenzoate, m.p. 56°; *p*-benzamido benzoate, m.p. 180—181°), and Δ^4 -hexahydroindene (III), b.p. 53°/11 mm.; the second base reacts more slowly with HNO₂ and gives 20% of hydrocarbon. The alcoholate of (I) in boiling decahydronaphthalene gives (II) quantitatively, and (II) is best prepared by treating the mixed bases with HNO₂ and isomerising the alcoholate of the crude product. Oxidation of (II) affords 2-carboxy-*cis*-cyclopentanepropionic acid, m.p. 99—100°. Ni-hydrogenation at 180—200° of 5-hydroxyindane, m.p. 54°, gives mainly the form (IV), b.p. 112—115°/13 mm., m.p. 20° (*H phthalate*, m.p. 144—145°; *H*, m.p. 146—147°, and *Me phthalate*, m.p. 54—58°, of the *Me ether*; *phenylurethane*, m.p. 74°; *p*-nitrobenzoate, m.p. 75°; *H succinate*, m.p. 47—48°), of 5-hydroxyhexahydrohydrindane with a little hydrocarbon and isomeric 5-OH-compound (V), new m.p. 43°, b.p. 106°/13 mm. (*H phthalate*, m.p. 106—107°; *oxalate*, m.p. 84°; *p*-nitrobenzoate, m.p. 61°). Ni-hydrogenation at 180° of 5-acetamidindane, m.p. 180°, gives the *Ac* derivative, m.p. (+2H₂O) 53° (anhyd.) 63°, of 5-amino hexahydrohydrindane (VI), b.p. 90°/12 mm., m.p. < -20° (*Bz* derivative, m.p. 145°; *Me carbamate*, m.p. 83°), and the *Ac* derivative, m.p. 108°, of the *isomeride* (VII) (*Bz* derivative, m.p. 165—166°; *Me carbamate*, m.p. 88°); the latter base with (?) 20% of the former is obtained by reduction of the mixed *cis*-hydrindane-5-oximes by Na-EtOH; the *Bz* derivative of this oxime undergoes spontaneous resolution in Et₂O or C₆H₆, giving the active *Bz* derivative, m.p. 140°, and thence an *oxime*, m.p. 59—60°; the *cis*-structure of this ketone is thus proved. With HNO₂ (VI) gives pure (V) and a little of a hydrocarbon, oxidised to *cis*-cyclopentane-1:3-diacetic acid (VIII); HNO₂ converts (VII) mainly into (IV), but some (V) and a hydrocarbon, oxidised to (VIII), are also formed.

R. S. C.

Intramolecular rearrangement. M. SOMMELET (Compt. rend., 1937, 205, 56—58; cf. A., 1923, i, 202).—CHPh₂·NMe₃·Br with Ag₂O in H₂O gives an aq. solution of CHPh₂·NMe₃·OH (I) from which H₂O is removed by distillation. (I) decomposes at 130—150° to give CHPh₂·OH, (CHPh₂)₂O, CHPh₂·OMe, NMe₃, NMe₂·CHPh₂ (cf. A., 1933, 262), and a small amount of (II) (below), formed by loss of 1 H₂O from (I). Conc. of an aq. solution of (I) over P₂O₅ finally leaves *o*-benzylbenzyl dimethylamine (II) [formed by dehydration of (I) followed by rearrangement], b.p. 189—190°/16 mm. (*methiodide*, m.p. 224—225°; *ethiodide*, m.p. 167°; *allyliodide*, m.p. 135°), converted by Ac₂O with formation of NMe₂·Ac into the *acetate*, b.p. 205°/22 mm., of *o*-benzylbenzyl

alcohol, b.p. 197—199°/19 mm. (*Ph carbamate*, m.p. 77°), which is oxidised (CrO₃) to *o*-benzylbenzoic acid, m.p. 116—117° (*amide*, m.p. 164—165·5°).

J. L. D.

Derivatives of 4-cyclohexyldiphenyl. III. F. R. BASFORD (J.C.S., 1937, 1440—1443).—4-cyclohexyldiphenyl (I) when nitrated (HNO₃-AcOH) affords 2- (II), m.p. 164·5°, and 4'-nitro-4-cyclohexyldiphenyl (III), m.p. 124°. (II) is oxidised (CrO₃-AcOH) to 2-nitrodiphenyl-4-carboxylic acid, and reduced (SnCl₂) to 2-amino-4-cyclohexyldiphenyl, m.p. 102° (*Ac*, m.p. 116°, and *Bz*, m.p. 158°, derivatives), whilst on dehydrogenation (Br) 2-nitro-1:4-diphenylbenzene, m.p. 125°, is formed, reduced (SnCl₂) to 2-amino-1:4-diphenylbenzene, m.p. 169° (*Bz* derivative, m.p. 144°). (III) is oxidised (Na₂CrO₇-aq. AcOH) to 4-nitrodiphenyl-4'-carboxylic acid, and reduced (SnCl₂) to 4'-amino-4-cyclohexyldiphenyl (IV) (*hydrochloride*, m.p. 90°; *Ac*, m.p. 225°, and *Bz*, m.p. 240°, derivatives), and on dehydrogenation (Br) yields 4'-nitro-1:4-diphenylbenzene, m.p. 211°. (IV) when diazotised and treated with KI affords 4-cyclohexyl-4'-diazonium *perbromide*, m.p. 105°, converted (hot EtOH) into 4'-bromo-4-cyclohexyldiphenyl. (I) with HNO₃ alone affords *trinitro*-4-cyclohexyldiphenyl, m.p. 235°, and with *p*-NO₂·C₆H₄·COCl in CS₂ with AlCl₃ yields 4'-*p*-nitrobenzoyl-4-cyclohexyldiphenyl, m.p. 175°, also formed by nitration of 4'-benzoyl-4-cyclohexyldiphenyl. 4-cyclohexyldiphenyl-4'-carboxylic acid with SOCl₂ affords the *chloride*, m.p. 109°. 4:4'-Dicyclohexyldiphenyl is nitrated to a (NO₂)₂-compound, m.p. 182°, reduced (Fe-HCl-EtOH) to a *diamine*, m.p. 225°.

J. D. R.

Nitration and halogenation of NN'-diphenylethylenediamine and its derivatives. II. A. E. SCHOUTEN (Rec. trav. chim., 1937, 56, 863—872; cf. this vol., 335).—Halogenation and nitration of (CH₂·NHPh)₂ (I) and its derivatives proceeds until all *o*- and *p*-positions are substituted, but only one NO₂ can be introduced into each Ph of the diacetylated *sec*-amines. NN'-Diphenylpiperazine (II) and its derivatives are converted into [2:4:6-(NO₂)₃C₆H₂·N(NO₂)·CH₂·]₂ etc. by abs. HNO₃. 1:3:4-C₆H₃Cl(NO₂)₂ and (CH₂·NH₂)₂ in EtOH give NN'-di-5-chloro-2-nitrophenylethylenediamine, m.p. 249°, the *Ac*₂ derivative, m.p. 229°, of which with abs. HNO₃ at 0° gives NN'-di-5-chloro-2:4:6-trinitrophenylethylenedinitroamine, m.p. 170°, explosive. Similarly are obtained NN'-di-5-bromo-2-nitrophenylethylenediamine, m.p. 260° (*Ac*₂ derivative, m.p. 209°), and NN'-di-5-bromo-2:4:6-trinitrophenylethylenedinitroamine, m.p. 187°, explosive. NN'-Di-2:4-dibromophenylethylenediamine, m.p. 138° (*Ac*₂ derivative, m.p. 227°), is obtained from (I) or its 2:2'- or 4:4'-Br₂-derivative by Br in AcOH and in CHCl₃ with Br gives NN'-di-2:4:6-tribromophenylethylenediamine, m.p. 129° (*Ac*₂ derivative, m.p. 234°). NN'-Di-2- and -4-nitrophenylethylenediamine and Br-AcOH give the known 4:4'-dibromo-2:2'- and 2:2'-dibromo-4:4'-dinitro-compounds, respectively. Cl₂ in AcOH without cooling degrades (I) to (CH₂·NH₂)₂, but at 0° in AcOH or CHCl₃ gives NN'-di-2:4:6-trichlorophenylethylenediamine, m.p. 104° (*Ac*₂ derivative, m.p. 243°). (CH₂·NPhAc)₂ and abs. HNO₃ at -10° give the 4:4'-(NO₂)₂-compound, which

resists further nitration, as also does the 2:2'-(NO₂)₂-compound. Diacet-NN'-di-*o*-bromophenylethylenediamide gives diacet-NN'-di-2-bromo-6-nitrophenylenediamide, m.p. 228°, the orientation of which is decided by deacetylation and further bromination to the 2:2':4:4'-tetrabromo-6:6'-dinitro-compound, which is also obtained by nitration and deacetylation of diacet-NN'-di-2:4-dibromophenylethylenediamide. Diacet-NN'-di-*p*-chloro- and -bromo-phenylethylenediamide give the known 2:2'-(NO₂)₂-compounds, and the 2:2':4:4'-tetrabromo-diacetamide gives diacet-NN'-di-2:4-dibromo-6-nitrophenylethylenediamide, m.p. 243°. (II), m.p. 164°, is prepared from (I) and (CH₂Br)₂ at 150°. *p*-C₆H₄Cl·NH₂, (CH₂Br)₂, and NaOAc at 140° give NN'-di-*p*-chlorophenylpiperazine, m.p. 239°. NN'-Di-*p*-bromophenylpiperazine, m.p. 227°, is obtained as a by-product in the prep. of (CH₂·NH·C₆H₄Br)₂. R. S. C.

Azo-dyes. III. A. ROLLETT [with R. BIRKNER, K. R. POSSELT, J. HOCHSTRASSER, and J. STERN] (Monatsh., 1937, 70, 425—430; cf. this vol., 97).—The absorption spectra of a no. of azo-dyes are determined in buffered solutions. Changes of colour are noted for dyes from NH₂Ph and many derivatives thereof with 1:4- and 1:5-NH₂·C₁₀H₆·SO₃H at *p*_H 3—5, with 1:6- and 1:7-NH₂·C₁₀H₆·SO₃H at *p*_H 4—5, with 1:4- and 1:7-OH·C₁₀H₆·SO₃H at *p*_H 9—10, with 1:5-OH·C₁₀H₆·SO₃H at *p*_H 8—9, and with 1:6-OH·C₁₀H₆·SO₃H at *p*_H 10. The *p*_H at which colour change occurs appears to be determined mainly by the C₁₀H₈ component of the dye. The ultra-violet adsorption spectra of α-C₁₀H₇·NH₂, 1-C₁₀H₇·SO₃H, 1:7-NH₂·C₁₀H₆·SO₃H, 1:4-OH·C₁₀H₆·SO₃H and -NMe₂·C₁₀H₆·SO₃H in buffered solutions are recorded. R. S. C.

Hydrazones and semicarbazides from *p*-thiocyanophenylhydrazine. Z. HORN (J. Pharm. Soc. Japan, 1935, 55, 880—887).—*p*-NH₂·C₆H₄·CNS is diazotised and reduced (SnCl₂) to *p*-thiocyanophenylhydrazine, m.p. 95—96°, isolated as the hydrochloride, decomp. 188°, which condenses with carbonyl compounds in 95% EtOH to give *p*-thiocyanophenylhydrazones of the following: COMe₂, m.p. 128.5—129°; AcCO₂H, m.p. 191—191.5°; CPhMe, m.p. 109—110°; PhCHO, m.p. 135—136°; *o*-, m.p. 172—173°, *m*-, m.p. 167°, and *p*-OH·C₆H₄·CHO, m.p. 154°; *o*-, m.p. 147—148°, and *p*-OMe·C₆H₄·CHO, m.p. 129—129.6°; heliotropin, m.p. 153—154°; veratraldehyde, m.p. 117°; isovanillin, m.p. 148—149°; 4-methoxy-3-ethoxybenzaldehyde, m.p. 113—114°; resorcyaldehyde, m.p. 191—192°; 2:4-(OMe)₂C₆H₃·CHO, m.p. 129—129.5°; *p*-tolualdehyde, m.p. 118—119°; cuminaldehyde, m.p. 140°; *o*-, m.p. 171°, *m*-, m.p. 161—162°, and *p*-NO₂·C₆H₄·CHO, m.p. 185—186°; *p*-NMe₂·C₆H₄·CHO, m.p. 158—159°; *m*-C₆H₄Cl·CHO, m.p. 125—125.5°; 2:5-OH·C₆H₃Cl·CHO, m.p. 217—218°; 2:3:5-OH·C₆H₂Cl₂·CHO, m.p. 223—224°; cinnamaldehyde, m.p. 138—140°; furfuraldehyde, m.p. 124°; β-C₁₀H₇·CHO, m.p. 207—208°; *d*-galactose, m.p. 181.5°; *d*-mannose, m.p. 185—186°; *l*-arabinose, m.p. 160—160.5°. The following are also described: acetonyl-*p*-thiocyanophenylhydrazine, m.p. 217°; 1-*p*-thiocyanophenylsemicarbazide, m.p. 217°, and its

4-*Ph*, m.p. 239—239.5°, 4-*o*-, m.p. 188—189°, *m*-, m.p. 230°, and *p*-tolyl, m.p. 238—239° derivatives, and the thio-derivatives of these, m.p. 187°, 190—191°, 163—164°, 177—178°, 170—171°.

CH. ABS. (r)

Reactions of thio-carbonyl chloride. V. With compounds containing the NH·NH₂ group. T. BECKETT and G. M. DYSON (J.C.S., 1937, 1358—1362; cf. this vol., 274).—CSCl₂ and arylhydrazines react thus: 3CSCl₂ + 2NH₂·NH·C₆H₄R →

CS[N(NCS)·C₆H₄R]₂ (A) + 6HCl;
(A) → C₆H₄R·NCS + C₆H₄R·N(NCS)₂ (B);
(B) → NH₂·C₆H₄R(NCS)₂ (C); (C) + CSCl₂ → C₆H₄R(NCS)₃ (D) + 2HCl. Compounds (D) are the products isolated, unless R = *p*-NO₂ or -Br; in the latter cases compounds (B) are obtained, but as sole products only if 10% of HCl is present. In 10% HCl NHPh·NH₂ and CScI₂ give PhNCS and 1:2:4-trithiocarbimidobenzene, m.p. 156°, which with NH₂Ph or C₆H₄Br·NH₂ in C₆H₆ gives 1:2:4-tris(phenyl-, m.p. 120°, or -4-bromophenyl-thiocarbamido)benzene, m.p. 183°, respectively, with dry EtOH gives 3:4-dithiocarbamidophenylthiourea, m.p. 74°, and with dry NH₃-C₆H₆ gives 1:2:4-trithiocarbamidobenzene, m.p. 170°, converted by HCl-C₆H₆ into H₂S and 2:5-dithiocarbamidoaniline, m.p. 149.5°. *s*-C₆H₃(NH₂)₃ and CScI₂ in 7% HCl give 1:3:5-trithiocarbimidobenzene, m.p. 143°. CScI₂ and NH₂·CO·NH·NH₂ in aq. Et₂O give *s*-dicarbamidothiocarbamide, m.p. 215° (decomp.), which gives colours or coloured ppts. with many metals; it detects 0.25 × 10⁻⁶ g. of Cu or 1 × 10⁻⁶ g. of Co in 50 ml. of H₂O. CScI₂ and aq. NH₂·CO·NH·NH₂·HCl afford 3:5-dithiocarbimidothiocarbonyldicarbamide (I), CS[N(NCS)·CO·NH₂]₂, m.p. 186—194° (decomp.), decomposed by Zn dust and dil. HCl to (CH₂O)₃ and by dil. alkali to H₂S, N₂H₄, CO₂, and NH₃, and converted by NH₂Ph, C₆H₄Me·NH₂, or C₆H₄Br·NH₂ into 2-thion-1-phenyl-, (II), m.p. 198°, *p*-tolyl-, m.p. 208°, and *p*-bromophenyl-dicarbamide, NHAr·CS·NH·NH·CO·NH₂, m.p. 202°, respectively, the two first-mentioned of these products being also obtained from NH₂·CO·NH·NH₂ and ArNCS. CScI₂ and NH₂·CO·NH·NHPh in aq. Et₂O give *s*-diphenyldicarbamidothiocarbamide, CS(NH·NH·CO·NHPh)₂, m.p. 223°, which gives a ppt. with Hg^{II} salts in concns. of >1 × 10⁻⁶; NH₂·CO·NH·NHPh in dil. HCl, however, gives 3:5-dithiocarbamido-1:1:7:7-tetraphenylthiocarbonyldicarbamide, CS[N(CNS)·CO·NHPh]₂, m.p. 133°, which with NH₂Ph in ligroin gives 3:5-bis(phenylthiocarbamido)-1:1:7:7-tetraphenylthiocarbonyldicarbamide, CS[N(CO·NHPh)₂·NH·CS·NHPh]₂, decomposed by hot 10% HCl into CO₂, H₂S, PhNCS, and NHPh·CO·NH·NHPh. (I) in hot abs. EtOH affords 3:5-dithiourethanocarbonyldicarbamide, CS[N(CO·NH₂)·NH·CS·OEt]₂, m.p. 30—32°, which with NH₂Ph-EtOH yields (II) and CS(NHPh)₂. NH₂·CO·CO·NH·NH₂·HCl and CScI₂ in H₂O give NN'-dithiocarbimido-NN'-dioxamylthiocarbamide, m.p. 223°, reduced by Zn dust and dil. acid to (CH₂O)₃, CO₂, H₂S, and NH₃, and converted by NH₂Ph into 1-oxamyl-4-phenylthiosemicarbazide, NHPh·CS·NH·NH·CO·CO·NH₂, m.p. 185.5°, which is also obtained from NH₂·CO·CO·NH·NH₂ and PhNCS in EtOH and is hydrolysed thereto by hot H₂O.

$\text{NH}_2 \cdot \text{NHMe} \cdot \text{H}_2\text{SO}_4$ gives NN'-dithiocarbimidodimethylthiocarbamide, m.p. 139°, decomposed by 20% NaOH and converted by NH_2Ph into $\text{CS}(\text{NHPh})_2$ and $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{NHMe}$, m.p. 153° (also obtained from $\text{NH}_2 \cdot \text{NHMe}$ and PhNCS). Dithiocarbimidodithiocarbamide, decomp. 196–200°, is obtained from CSCl_2 and aq. N_2H_4 or $\text{CS}(\text{NH} \cdot \text{NH}_2)_2$ in 10% HCl, and with NH_2Ph or $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ gives $\text{CS}(\text{NHAr})_2$ and dithio-*p*-urazine, $\text{CS} \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ \text{NH} \cdot \text{NH} \end{smallmatrix} \text{CS}$, m.p. 202–203°, also obtained from K ethylxanthate and $\text{CS}(\text{NH} \cdot \text{NH}_2)_2$ in EtOH. $\text{NH}_2 \cdot \text{NPh}_2 \cdot \text{HCl}$ and CSCl_2 give N-thiocarbimidodiphenylamine, m.p. 63°. $\text{NH}_2 \cdot \text{NPhMe}$ in 5% HCl gives N-thiocarbimidophenylmethylamine, an oil, which with NH_2Ph yields $\text{NHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{NPh}_2$, $\text{CO}(\text{NHPh})_2$, and PhNCS . *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH}_2$ in 10% HCl gives NN'-dithiocarbimidobis-*p*-nitrophenylthiocarbamide (A; R = NO_2), cryst., sol. in 2*N*-NaOH, reacting with benzidine, reduced by Sn-HCl to NH_4Cl , H_2S , $(\text{CH}_2\text{O})_3$, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, and converted by NH_2Ph into NN'-diphenylthiocarbimidobis-*p*-nitrophenylthiocarbamide, m.p. 143°, which is hydrolysed by HCl. $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{NH}_2$ and CSCl_2 give 3:5-dithiocarbimidodithiocarbonyldithiocarbamide, $\text{CS}[\text{N}(\text{NCS}) \cdot \text{CS} \cdot \text{NH}_2]_2$, m.p. 240–250° (decomp.), which with NH_2Ph gives $\text{CS}(\text{NHPh})_2$ and dithiourazole. R. S. C.

Influence of substituents on the coupling of phenols with diazonium salts. D. H. RICHARDSON (J.C.S., 1937, 1363–1365).—By coupling 1 mol. of *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{HSO}_4$ with 1 mol. each of two phenols and determining the halogen in the dye, it is shown that relative rates of coupling for $\text{C}_6\text{H}_4\text{R} \cdot \text{OH}$ are R = *o*-Cl 0.51, *m*-Cl 0.36, *o*-Br 0.84, *m*-Br 0.63, H 1, *o*-I 1.13, *m*-I 1.24, *o*-Me 6.6, and *o*-OMe 28.4. Thus, Br has a greater inductive effect than Cl, and I has an activating effect; the *m*- (coupling) position is more powerfully activated by meso- and electro-meric (OMe) than by inductive (Me) effects; from results with $\text{C}_6\text{H}_5\text{Cl}_2 \cdot \text{OH}$ and $\text{C}_6\text{H}_5\text{Br}_2 \cdot \text{OH}$ it is deduced that the deactivating effect reaches the coupling position by one side of the C_6H_5 ring at one time. R. S. C.

Preparation of *m*-tolyl isopropyl ether from *m*-cresol and isopropyl chloride. T. BOYD and E. F. DEGERING (J. Amer. Chem. Soc., 1937, 59, 1399).—*m*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{OPr}^i$ (23–27 g.) is prepared by slowly heating *m*-cresol (25 g.), Pr^iCl (30 c.c.), and NaOH (9.2 g.) to 150° in an autoclave, maintaining at 150–160° for 3 hr., and extracting with C_6H_6 . A. LI.

Cleavage of diphenyl ethers by sodium in liquid ammonia. II. *meta*-Substituted diphenyl ethers. A. L. KRANZFELDER, J. J. VERBANC, and F. J. SOWA (J. Amer. Chem. Soc., 1937, 59, 1488–1490; cf. this vol., 239).—Cleavage of the following ethers, ROR' , by Na in liquid ammonia gives the stated % of ROH, the residue being $\text{R}'\text{OH}$: R = Ph, $\text{R}' = 3 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4$, 28, $3 \cdot \text{OMe} \cdot \text{C}_6\text{H}_4$, 53, $3 \cdot \text{C}_6\text{H}_4\text{Me}$, 38, or $3 \cdot \text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4$, 64; R = $2 \cdot \text{OMe} \cdot \text{C}_6\text{H}_4$, $\text{R}' = 3 \cdot \text{OMe} \cdot \text{C}_6\text{H}_4$, 24; R = $3 \cdot \text{OMe} \cdot \text{C}_6\text{H}_4$, $\text{R}' = 4 \cdot \text{C}_6\text{H}_4\text{Me}$, 8; R = $2 \cdot \text{C}_6\text{H}_4\text{Me}$, $\text{R}' = 3 \cdot \text{C}_6\text{H}_4\text{Me}$, 47; R = $3 \cdot \text{C}_6\text{H}_4\text{Me}$, $\text{R}' = 4 \cdot \text{C}_6\text{H}_4\text{Me}$, 23%. These and previous results are interpreted on the basis of electromeric and inductive effects, Na or the

electron concerned being considered as a nucleophilic reagent; the explanation is not entirely satisfactory for *o*-substituents. The following substituents strengthen the link between O and substituted Ph: *o*- > *m*-Me > *m*- NH_2 > *p*-Me > *p*-OMe > *o*- > *p*- NH_2 ; the following weaken this linking: *m*- > *o*-OMe > *m*- > *o*- > *p*- CO_2Na . The following are described: Ph 3-nitro-, b.p. 174°/8 mm., 3-amino-, b.p. 194°/10 mm., 3-methoxy-, b.p. 127°/2 mm., 3-carbonyl- (I), m.p. 139°, 2:3-, b.p. 152°/2 mm., and 3:4-dimethoxy-phenyl, b.p. 163°/22 mm., and vic-, b.p. 152°/2 mm., m.p. 48.5°, and as-*o*-xylyl ether, b.p. 174°/4 mm. All these require 2 Na for cleavage, except (I), which requires 3. R. S. C.

Derivatives of *o*-hydroxybenzylsulphonic acid. E. A. SHEARING and S. SMILES (J.C.S., 1937, 1348–1351).—The reaction (A), $\text{CH}_2(\text{C}_{10}\text{H}_6 \cdot \text{OH})_2 + \text{Na}_2\text{SO}_3 \rightleftharpoons \text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na} \text{ (I)} + \text{C}_{10}\text{H}_7 \cdot \text{ONa}$, is shown to be reversible and may be used to prepare *as*-di-2-hydroxynaphthyl-1-methanes, but not all dihydroxynaphthylmethanes are thus cleaved. When $\beta\text{-C}_{10}\text{H}_7 \cdot \text{OH}$, CH_2O , and Na_2SO_3 react to form (I), reaction occurs partly by (A) and partly by way of $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CH}_2 \cdot \text{OH}$, which then reacts with Na_2SO_3 . Compounds, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, are prepared, usually in small yield, from *o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OH}$ (not $\text{CH}_2\text{Ph} \cdot \text{OH}$) and NaHSO_3 or from the phenols, CH_2O , and Na_2SO_3 ; they are characterised by conversion into benzylsulfones, *o*- $\text{Ar} \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{SO}_2$. R in 2:1-

$\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CH}_2\text{R}$ is unusually mobile, which is paralleled by fission of di-2-hydroxynaphthyl 1-sulphide (II) by Na_2SO_3 to $\beta\text{-C}_{10}\text{H}_7 \cdot \text{OH}$ and *Na* 2-hydroxynaphthyl-1-thiolsulphonate, +0.5 H_2O [which reform (II) in hot alkali], and by alkaline reduction of (II) to $\beta\text{-C}_{10}\text{H}_7 \cdot \text{OH}$ and 2:1- $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SH}$. The following are described: di-6-bromo-2-hydroxynaphthyl-1-methane, m.p. 240°, stable to Na_2SO_3 ; 3-, m.p. 200° (decomp.), and 6-bromodi-2-hydroxynaphthyl-1-methane, m.p. 210° (decomp.); Na and Pb 6-bromo-2-hydroxynaphthyl-1-methanesulphonate; Na 2-hydroxyphenyl-, 4-hydroxy-*p*-tolyl-3-, 4-hydroxy-*m*-xylyl-5-, and 2-hydroxy-*p*-xylyl-5-methanesulphonate (Ba salt); 5-methyl-, m.p. 91.5°, and 5:7-dimethylbenzylsulfone, m.p. 92.5°; phenyl-, m.p. 87°, *p*-tolyl-, m.p. 103°, and 2-hydroxy-2'-nitrophenyl-3:5-dimethylbenzylsulphone, m.p. 168°, unstable to alkali. $\beta\text{-C}_{10}\text{H}_7 \cdot \text{OH}$ with 4:1:3:5- $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CH}_2\text{Cl}$ in C_6H_6 or 4:1:3:5- $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CH}_2 \cdot \text{OH}$ in AcOH gives 1-2'-hydroxy-3':5'-dimethylbenzyl-2-naphthol, m.p. 175° (Ac_2 derivative, m.p. 99°). R. S. C.

Fused carbon rings. XII. A simple synthesis of derivatives of decahydronaphthalene from cyclohexanone, and observations on cyclohexanespirobutyrolactone and allied compounds. R. P. Linstead, A. B.-L. Wang, J. H. Williams, and (in part) K. D. Errington. XIII. Synthesis of derivatives of decahydronaphthalene containing an angular methyl group. R. P. Linstead, A. F. Millidge, and A. L. Walpole (J.C.S., 1937, 1136–1140, 1140–1145).—XII. 1- Δ^7 -Butenylcyclohexanol (I), b.p. 95–96°/10 mm. [obtained from cyclohexanone and $\text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_2 \cdot \text{MgBr}$ (II)], is dehydrated by $\text{H}_2\text{C}_2\text{O}_4$ at 125–135° to 1- Δ^7 -butenyl-

Δ^1 -cyclohexene (III), b.p. 60–62°/10 mm., and by $P_2O_5-H_3PO_4$ at 160° to a mixture of (III) and $\Delta^9:10$ -octahydronaphthalene (A., 1929, 76), also obtained from *trans*-decahydro- β -naphthol and $P_2O_5-H_3PO_4$, or from *trans*- Δ^2 -decahydronaphthalene and P_2O_5 . With $AcOH-Ac_2O-H_2SO_4$, (I) gives *cis*-decahydro- β -naphthol, also obtained from (III) and $AcOH-H_2SO_4$. That (I) has a Δ^7 -structure is shown by oxidation ($KMnO_4$) to γ -cyclohexanespirobutyrolactone (IV), new m.p. 20–20.5°, new b.p. 130–133°/12 mm. (cf. A., 1928, 289). This is also prepared (H_2SO_4) from β -cyclohexylidenepropionic acid (V), new m.p. 47–48°, obtained from cyclohexanecarbaldehyde (VI), $CH_2(CO_2H)_2$, and $N(CH_2-CH_2-OH)_3$. Sircar's (IV) and (V) (*loc. cit.*) are contaminated with one another, and, contrary to his statement, β -cyclohexylacrylic acid (VII) [from (VI), $CH_2(CO_2H)_2$, and C_5H_5N] when boiled with 40% aq. KOH gives a mixture of (V) (54%) and (VII). Boiling H_2O hydrolyses (IV) only very slightly.

XIII. 2-Methyl-1- Δ^7 -butenylcyclohexanol (A., 1936, 846) and $AcOH-Ac_2O-H_2SO_4$ give a mixture containing *cis*-9-methyldecahydro- β -naphthol (VIII), m.p. 72°, oxidised by HNO_3 to *cis*-1-methylcyclohexane-1:2-diacetic acid (IX), m.p. 190°. The last when distilled with $Ba(OH)_2$ yields *cis*-8-methyl-2-hydrindanone (X), m.p. 39–40°, b.p. 105°/14 mm. (semicarbazone, m.p. 220°), which is oxidised to 1-methylcyclohexane-1-carboxylic-2-acetic acid. Oxidation of (VIII) by CrO_3 yields *cis*-2-keto-9-methyldecahydronaphthalene (XI), m.p. 17–18°, b.p. 122–123°/14 mm. (semicarbazone, m.p. 210–212°). The structure of (XI) and of the *cis*-3-keto-9-methyl (*i.e.*, 2-keto-10-methyl) isomeride (XII) (this vol., 197) is established by their common oxidation to (IX). Both (XI) and (XII) similarly belong to the same stereochemical series, regarded as *cis*. The mixture from which (VIII) is removed is oxidised to (XI). Oxidation of the impure alcohol with HNO_3 gives (IX), with a C_{11} -acid, m.p. 164° (cf. A., 1936, 846), probably *trans*-1-methylcyclohexane-1:2-diacetic acid. Clemmensen reduction of (XI) gives *cis*-9-methyldecahydronaphthalene (XIII), m.p. –22°, b.p. 79°/11 mm., and dehydration of (VIII) *cis*-9-methyloctahydronaphthalene (XIV), b.p. 78–80°/12 mm. which on oxidation gives (IX), and thus contains the Δ^2 -form. The evidence for the *cis*-configuration of the above series lies in the physical properties of (XIII), (XI), *cis*-8-methylhydrindanone, m.p. 10–14°, b.p. 56°/10.5 mm. [obtained by Clemmensen reduction of (X)], and (XIV), which all have high *d* and *n*, and normal [*R*], and in the parallel formation of a *cis*-compound from (I). The methyl-octahydronaphthalenes obtained (A., 1936, 846) by direct cyclisation of methylbutenylcyclohexanols are mixtures of isomerides, perhaps containing *trans*-9-methyl- $\Delta^4:10$ -octahydronaphthalene. 2:6-Dimethyl- Δ^7 -butenylcyclohexanol, b.p. 100–105°/10 mm. [obtained from 2:6-dimethylcyclohexanone (A., 1931, 1303) and (II)], is dehydrated ($P_2O_5-H_3PO_4$) to $\Delta^7:1:10(=4:9)$ -dimethyloctahydronaphthalene, b.p. 86–90°/10 mm., which is hydrogenated to 1:10(=4:9)-dimethyldecahydronaphthalene, b.p. 84–85°/10 mm. (of which the physical properties show that it is mainly *cis*), which with $AlCl_3$ is converted into the *trans*-form, b.p. 76–78°/10 mm. E. W. W.

Reaction between formaldehyde and naphthols.

A. CASTIGLIONI (Gazzetta, 1937, 67, 324–326).—The product from CH_2O and α - $C_{10}H_7\cdot OH$ in conc. HCl is regarded as *di*-(α -hydroxynaphthyl)carbinol, and that from β - $C_{10}H_7\cdot OH$ (cf. A., 1935, 877) as *iso*-1:2:7:8-dibenzoxanthene (cf. A., 1934, 779). E. W. W.

Synthesis of ethers of eugenol and isoeugenol.

S. ISHIKAWA and M. MATSUHASHI (Sci. Rep. Tokyo Bunrika Daigaku, 1937, 3, A, 165–172).—Eugenol β -phenylethyl ether, b.p. 192–196°/5 mm., m.p. 29°, obtained in 37% yield from eugenol (I) and $CH_2Ph\cdot CH_2Cl$ with KOH in EtOH or K_2CO_3 in $COMe_2$, is converted by KOH–EtOH at 100° into styrene and isoeugenol (II). *iso*Eugenol β -phenylethyl ether, b.p. 210–212°/6 mm., is obtained from (II), $CH_2Ph\cdot CH_2Cl$, and KOH–EtOH. Eugenol γ -phenylpropyl ether, b.p. 200–205°/4 mm., from (I), $CH_2Ph\cdot CH_2\cdot CH_2Cl$, and KOH–EtOH, is isomerised by alkali to isoeugenol γ -phenylpropyl ether, b.p. 200–204°/3 mm., which gives MeCHO when ozonised. (I), $CHPh\cdot CH\cdot CH_2Cl$, and KOH–EtOH give *o*-cinnamylisoeugenol, b.p. 200–207°/3 mm. (phenylurethane, m.p. 149°), ozonised to PhCHO and MeCHO. H. W.

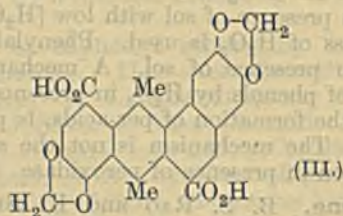
Oxidation of phenols by means of hydrogen peroxide in presence of inorganic catalysts.

B. C. KAR (J. Indian Chem. Soc., 1937, 14, 291–319).—The kinetics of the oxidation by means of H_2O_2 in presence of tungstic acid sol (I) of quinol, pyrogallol, guaiacol, and a mixture of p - $C_6H_4(NH_2)_2$ and α - $C_{10}H_7\cdot OH$ have been studied, the temp., p_H , and concns. of H_2O_2 , sol, and substrate being varied. In some cases molybdic and vanadic acid sols have also been studied. The oxidation of pyrocatechol, *p*-cresol, tyrosine, and tryptophan by H_2O_2 in presence of (I) has also been studied. The results are compared with those obtained with H_2O_2 in presence of peroxidases (cf. lit.). All phenolic substances can be oxidised by H_2O_2 in presence of one of the above-mentioned sols, CO_2 being produced when high concns. of H_2O_2 and sol are used. KCN and $HgCl_2$ (strong poisons for peroxidases), heat, and ultra-violet light have little effect on the activity of the sols. At low $[H_2O_2]$ the products obtained in the presence of sol are the same as those obtained in presence of peroxidase. Tincture of guaiacum gives a blue colour also with H_2O_2 in presence of sols. The optimum p_H and temp. coeff. of the oxidation in presence of peroxidase and of sol are not the same. No NH_3 is evolved in the oxidation of tyrosine in presence of sol with low $[H_2O_2]$, but only when excess of H_2O_2 is used. Phenylalanine is not oxidised in presence of sol. A mechanism for the oxidation of phenols by H_2O_2 in presence of the sols, involving the formation of per-acids, is proposed and discussed. The mechanism is not the same as that for oxidation in presence of peroxidase. H. G. M.

β -Asarone. B. S. RAO and K. SUBRAMANIAM (J.C.S., 1937, 1338–1340).— β - (I), b.p. 162–163°/12 mm., and α -asarone (II), m.p. 62–63°, b.p. 167–168°/12 mm., are *cis-trans* isomerides. Both are polymerised by HCl with development of a blue colour. KOH at 200–220° converts (I) into (II). Short treatment of (I) with SeO_2 in hot EtOH gives (II), but longer treatment gives a complex mixture

including 2:5-dimethoxypropenylbenzene (*picrate*, m.p. 87°; *nitrosite*, m.p. 118°). Reduction of (I) by Na-EtOH gives 1:2:4:5-C₆H₂Pr^a(OMe)₃. Br and (I) in CS₂-Et₂O at -20° give mainly a liquid *dibromide* with a little asarone dibromide, m.p. 82—83°, both converted by Cu in C₆H₆ into diasarone monobromide, m.p. 122°. HNO₃ converts (I) and (II) into asarone *ψ*-nitrosite. Hg(OAc)₂ and (I) give α-2:4:5-trimethoxyphenylpropane-αβ-diol, an oil, whereas (II) gives an oily *isomeride*; both glycols are converted into a *substance*, C₂₁H₃₀O₈, m.p. 204—205°, by distillation at 4 mm. or by treatment with Ac₂O at <40°. R. S. C.

Synthesis of 6:7-methylenedioxy-1:4-dimethylphenanthrene and of certain substituted 9:10-dimethyl-1:2:5:6-dibenzanthracenes. R. B. AKIN and M. T. BOGERT (J. Amer. Chem. Soc., 1937, 59, 1564—1567).—1:4:2-C₆H₃Me₂·CH₂·CO₂K and 6-nitropiperonal (I) in Ac₂O at 105—110° give 2-nitro-4:5-methylenedioxy-α-p-xylylcinnamic acid, m.p. 209.4—209.9° (*Me* ester, m.p. 157.5—158°), reduced (FeSO₄-NH₃) to the *NH*₂-acid, m.p. 216—217°, which yields (Pschorr) 6:7-methylenedioxy-1:4-dimethylphenanthrene-10-carboxylic acid, m.p. 221—222°, converted by basic Cu carbonate (less well by Cu) in quinaldine into 6:7-methylenedioxy-1:4-dimethylphenanthrene, m.p. 166.5—167° (*picrate*, m.p. 155—158°, dissociates in solvents). Attempts to open the CH₂O₂ ring of this ether failed. 2:5-Di(cyanomethyl)-p-xylene (prep. from the dichloride by NaCN in aq. EtOH), m.p. 157.8—158.3°, affords p-xylylene-2:5-diacetic acid (II), m.p. 254—255° (*Me*₂ ester, m.p. 61°), and thence (condensation with o-NO₂-C₆H₄·CHO, reduction, and Pschorr reaction) di-o-nitrobenzylidene-p-xylylene-2:5-diacetic acid, m.p. 330° (decomp. from 290°), the corresponding (*NH*₂)₂-acid, decomp. 293—296° (softens at 285°), and 9:10-dimethyl-1:2:5:6-dibenzanthracene-4:8-dicarboxylic acid, m.p. >350° (sinters at 335°), decarboxylated by Cu in quinaldine to 9:10-dimethyl-1:2:5:6-dibenzanthracene, m.p. 203—204°. Similar reactions, starting from (I) and (II), lead to di-(2'-nitro-4':5'-methylenedioxybenzylidene)-p-xylylene-2:5-diacetic acid, darkens at >300° (*Na*₂ salt), the corresponding (*NH*₂)₂-acid, m.p. 350° (sinters and darkens at 295°; *Ac*₂ derivative, m.p. >350°, darkens at >300°), 9:10-dimethyl-1:2:5:6-di-(3':4'-methylenedioxybenz)anthracene-4:8-dicarboxylic acid (III), darkens at >300°, m.p. >350°, and



9:10-dimethyl-1:2:5:6-di-(3':4'-methylenedioxybenz)-anthracene, m.p. 279—281° (sinters at 261—266°), the CH₂O₂ rings of which could not be opened by AlBr₃. M.p. are corr. R. S. C.

Reactions of sodium mono- and di-sulphides with 1-chloro-2-nitro-, 2-chloro-1-nitro-, and

1-chloro-4-nitro-naphthalene. H. H. HODGSON and E. LEIGH (J.C.S., 1937, 1352—1353).—1:2-, m.p. 80.5—81°, 2:1-, m.p. 99—100°, and 1:4-C₁₀H₆Cl·NO₂, m.p. 87—87.5° (2 mols.), and Na₂S₂ (1 mol.) in hot EtOH give 1:13, 1:12, and 1:12 mixtures, respectively, of dinitrodinaphthyl mono- and di-sulphides; in C₆H₆ the latter are almost the sole products; with Na₂S in EtOH the proportions are 1:1.2, 1:0.8, and 1:1.5, respectively, the disulphide being formed from the thiol which is the initial product. The Na salts of the thiols and C₁₀H₆Cl·NO₂ give 1:1'-dinitro-2:2'-, m.p. 203—204°, 2:2'-, m.p. 204—205°, and 4:4'-dinitro-1:1'-dinaphthyl sulphide, m.p. 239—240°. 4:4'- and 2:2'-Dinitro-1:1'- and 1:1'-dinitro-2:2'-dinaphthyl disulphide melt at 188—189°, 176—177°, and 188—190°, respectively. R. S. C.

Isomerisation of methylenecyclohexane oxide to hexahydrobenzaldehyde and deamination of the corresponding amino-alcohol to cycloheptanone. M. TIFFENEAU, P. WEILL, and B. TCHOUBAR (Compt. rend., 1937, 205, 54—56).—Methylenecyclohexane (cf. A., 1906, i, 563) with BzO₂H affords epoxymethylcyclohexane (I), b.p. 103—104°, which is isomerised by ZnCl₂ at 100° to hexahydrobenzaldehyde. When (I) is heated with excess of conc. aq. NH₃ in a sealed tube it affords 1-hydroxy-1-cyclohexylmethylamine, b.p. 106°/16 mm. (hydrochloride, m.p. 205°), which with NaNO₂ in dil. AcOH at room temp. gives cycloheptanone after a semipinacolin change and a rupture of the ring (cf. this vol., 241; A., 1935, 1240; 1920, i, 2; 1913, i, 181).

J. L. D.

Addition of hydracids to the epoxides, and hypohalogenous acids to the ethylenic derivatives, methylenecyclohexane, and methylcyclohexene and their epoxides. M. TIFFENEAU, P. WEILL, and B. TCHOUBAR (Compt. rend., 1937, 205, 144—146; cf. A., 1932, 394; 1923, i, 8; 1906, i, 228).—Methylenecyclohexane adds HOCl to give 1-chloro-1-hydroxymethylcyclohexane (I), m.p. 75° (in which Cl is linked to the more substituted C), which is converted by aq. KOH into the *epoxide* (II), b.p. 42°/15 mm., and by MgEtBr into C₆H₁₁·CHO. (II) reacts with dry HCl in cold Et₂O to give (I). 1-Methyl-1:2-epoxycyclohexane with dry HCl in cold Et₂O and 1-methyl-Δ¹-cyclohexene with HOCl afford *cis*- and *trans*-2-chloro-1-methylcyclohexanol (III) (in which Cl is linked to the less substituted C) respectively. Removal of Cl with Mg from the *cis*-form gives rise mainly to 2-methylcyclohexanone and a little acetylcyclopentane, which is the sole product obtained in a similar reaction with the *trans*-form (cf. A., 1934, 1098).

J. L. D.

Preparation of 5-bromo-2-methoxybenzyl alcohol and 5-bromo-2-methoxybenzaldehyde. R. QUELET and M. PATY (Compt. rend., 1937, 205, 146—148; cf. this vol., 146).—p-C₆H₄Br·OMe with CH₂O, dry HCl, and ZnCl₂ affords 5-bromo-2-methoxybenzyl chloride (I), converted by boiling aq. K₂CO₃ into 5-bromo-2-methoxybenzyl alcohol (II), m.p. 72° (phenylurethane, m.p. 121.5°). (I) with boiling NaOAc affords 5-bromo-2-methoxybenzyl acetate, m.p. 64°, converted by boiling aq. EtOH-KOH into (II). (I)

when boiled with $\text{Cu}(\text{NO}_3)_2$ and AcOH [or when boiled with aq. $\text{EtOH}-(\text{CH}_2)_6\text{N}_4$] affords 5-bromo-2-methoxybenzaldehyde, m.p. 114.5° (*semicarbazone*, m.p. $244-245^\circ$), and a little 5-bromo-2-methoxybenzoic acid. J. L. D.

Hydrocarbons, halogen derivatives, ethers, and esters derived from tetrahydroionol. J. KANDEL (Compt. rend., 1937, 205, 63-65; cf. this vol., 108).— β -Ionone (1 mol.) absorbs 2 H (Ni) under pressure at room temp.; at 50° 4-6 H is absorbed and at $230-240^\circ$ reduction is complete to tetrahydroionol (I), also obtained from α -ionone. At 290° (I) loses H_2O and is then further hydrogenated to 1:3:3-trimethyl-2-butylcyclohexane (*tetrahydroionane*), b.p. $95-96^\circ/14$ mm. (I) with NaHSO_4 affords *dihydroionane*, b.p. $98.5^\circ/16.5$ mm., and with dry HCl at 100° , or with HBr , or with I-red P it affords the corresponding *Cl-*, b.p. $128-128.5^\circ/17$ mm., *Br-*, b.p. $138.5-139^\circ/16$ mm., and *I-*, b.p. $151.5-152^\circ/14$ mm., derivatives, respectively. The Na derivative of (I) with the appropriate alkyl iodide affords the *Me*, b.p. $118^\circ/13.5$ mm., *Et*, b.p. $123.5^\circ/13$ mm., and *Pr*^{*a*}, b.p. $131-132^\circ/15$ mm., ethers, respectively. (I) with trioxymethylene and dry HCl gives the *chloromethyl* derivative, b.p. $150-151^\circ/15$ mm., converted by MgEtBr and $\text{MgPr}^{\text{a}}\text{Br}$ into the *Pr*^{*a*}, b.p. $133-134^\circ/14$ mm. and *Bu*^{*b*}, b.p. $142-143^\circ/15$ mm., ethers, respectively. (I) with $\text{HCO}_2\text{H}-\text{Ac}_2\text{O}$ gives the *formate*, b.p. $134-134.5^\circ/15$ mm., with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}-\text{C}_5\text{H}_5\text{N}$ the *H phthalate*, m.p. 79° (*allophanate*, m.p. 164°), with AcCl , PrCl , and BzCl , the acetate, b.p. $141.5-142^\circ/15.5$ mm. (cf. A., 1916, i, 16), *propionate*, b.p. $151.5-152^\circ/15.5$ mm., and *benzoate*, b.p. $210.5-211^\circ/13$ mm., respectively. J. L. D.

Reducing and condensing action of alkali benzyloxides on ketones, aldehydes, and $\alpha\beta$ -unsaturated alcohols. P. MASTAGLI (Compt. rend., 1937, 204, 1656-1658; cf. this vol., 102).—Michler's ketone with $\text{N-CH}_2\text{Ph}\cdot\text{OK}$ at 210° affords the hydrol, $\text{CH}_2\text{Ph}\cdot\text{OH}$ being oxidised to BzOH . COPhMe under similar conditions affords $\alpha\gamma$ -*diphenylpropanol* (80%), b.p. $194^\circ/15$ mm. (*allophanate*, m.p. 99°), and $\alpha\gamma$ -*diphenyl- β -benzyl-n-propyl alcohol* (20%), b.p. $254-255^\circ/15$ mm., oxidised (CrO_3) to the corresponding ketones. Similarly, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ affords γ -*phenyl- α -p-tolylpropyl alcohol*, b.p. $200^\circ/13$ mm. (*allophanate*, m.p. 111°). $\beta\text{-C}_{10}\text{H}_7\cdot\text{COMe}$ similarly affords γ -*phenyl- α -2-naphthylpropyl alcohol*, m.p. 63° , oxidised by CrO_3 to the corresponding ketone, m.p. 93° and by HNO_3 to $\beta\text{-C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$. Cinnamyl alcohol similarly affords γ -*phenyl- β -benzyl-n-propyl alcohol*, b.p. $202^\circ/15$ mm. (*allophanate*, m.p. 140°), oxidised to β -*phenyl- α -benzylpropionic acid*, m.p. 89° . α -Butyl-, -amyl-, and -hexyl-cinnamaldehydes with $\text{N-CH}_2\text{Ph}\cdot\text{ONa}$ (the K derivative causes reduction) at 100° afford α -butyl-, -amyl-, b.p. $162^\circ/12$ mm. (*allophanate*, m.p. 160°), and -hexyl-cinnamyl alcohol, respectively. Many straight-chain aldehydes similarly afford two products, one obtained as a result of an aldol condensation and the other by the introduction of CH_2Ph into the aldehyde. Thus $\text{Pr}^{\text{a}}\text{CHO}$ gives β -*ethylhexanol*, b.p. $85^\circ/16$ mm. (*allophanate*, m.p. 125°), and β -*benzyl-n-butyl alcohol*, b.p. $134^\circ/15$ mm. (*allophanate*, m.p. 134°); hexalde-

hyde gives β -*butyloctanol*, b.p. $132^\circ/15$ mm. (*allophanate*, m.p. 119°), and β -*benzyl-n-hexyl alcohol*, b.p. $155^\circ/15$ mm. (*allophanate*, m.p. 144°); octaldehyde gives β -*hexyldecyl*, b.p. $177^\circ/15$ mm. (*allophanate*, m.p. 90°), and β -*benzyl-n-octyl alcohol*, b.p. $176^\circ/15$ mm. (*allophanate*, m.p. 124°); nonaldehyde gives β -*heptylundecyl*, b.p. $198^\circ/15$ mm. (*allophanate*, m.p. 80°), and β -*benzyl-n-nonyl alcohol*, b.p. $186^\circ/15$ mm. (*allophanate*, m.p. 115°); decaldehyde gives β -*octyldodecyl*, b.p. $215^\circ/15$ mm. (*allophanate*, m.p. 69°), and β -*benzyl-n-decyl alcohol*, b.p. $200^\circ/15$ mm. (*allophanate*, m.p. 117°); undecaldehyde gives β -*nonyltridecyl*, b.p. $235^\circ/15$ mm. (*allophanate*, m.p. 80°), and β -*benzyl-n-undecyl alcohol*, b.p. $207^\circ/14$ mm. (*allophanate*, m.p. 97°); dodecaldehyde gives β -*decyltetradecyl*, b.p. $250^\circ/15$ mm. (*allophanate*, m.p. 72°), and β -*benzyl-n-dodecyl alcohol*, b.p. $221^\circ/15$ mm. (*allophanate*, m.p. 109°); Δ^1 -undecenaldehyde gives β -*nonenetridecyl*, b.p. $235^\circ/15$ mm. (*allophanate*, m.p. 75°), and β -*benzyl-n-undecenyl alcohol*, b.p. $211^\circ/15$ mm. (*allophanate*, m.p. 109°). J. L. D.

Addition of hypochlorous acid to phenylbutadiene and isomerisation of the corresponding epoxide to phenylcrotonaldehyde. D. ABRAGAM and Y. DEUX (Compt. rend., 1937, 205, 285-286; cf. this vol., 225).—Phenylbutadiene (I), obtained from $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ and MgMeBr or $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ and MgPhBr , with cold aq. HOCl affords the chlorohydrin of phenylvinyl glycol, converted by KOH in Et_2O into the epoxide (II) (cf. A., 1930, 769), the structure of which is indicated by its reduction (H_2 -Raney Ni) to α -phenyl-n-butyl alcohol, dehydrogenated (Cu at $280-300^\circ$) to COPhPr^{a} . (II) at 250° and 16 mm. affords $\text{CHMe}\cdot\text{CPh}\cdot\text{CHO}$ (cf. this vol., 246). J. L. D.

Action of magnesium ethyl bromide and of magnesium bromide on $\beta\beta$ -dimethylstyrene oxide. M. POCTIVAS and (MLLE.) B. TCHOUBAR (Compt. rend., 1937, 205, 287-288; cf. A., 1932, 392; 1921, i, 788).— $\beta\beta$ -Dimethylstyrene oxide (I) with $\text{MgBr}_2\cdot\text{Et}_2\text{O}$ at $<100^\circ$ affords mainly (90%) $\text{CPhMe}_2\cdot\text{CHO}$ (II) and a little (10%) β -phenylbutan- γ -one (III). Interaction of (I) with MgEtBr affords a mixture of approx. equal amounts of α -phenyl- $\beta\beta$ -dimethyl-n-butyl alcohol and γ -phenyl- β -methyl-n-pentan- β -ol, oxidised (CrO_3) to PhCHO , BzOH , and COPhEt but no COPhMe , which is obtained by oxidising a mixture of the alcohols obtained synthetically from (II) and (III) with MgEtBr . Thus, the rate of isomerisation of (I) by MgBr_2 is much slower than its rate of reaction with MgEtBr . J. L. D.

Stereochemical structure. VIII. Stereochemical relationship of the α - and the β -forms of substituted hydrobenzoins. (a) **Ethylhydrobenzoin (α -form).** R. ROGER (J.C.S., 1937, 1048-1051).—Attempted reduction of the stereoisomeric compounds of formula $\text{OH}\cdot\text{CHPh}\cdot\text{CPhEt}\cdot\text{OH}$ to $\text{CH}_2\text{Ph}\cdot\text{CPhEt}\cdot\text{OH}$ was not successful; mild agents were without action, and HI caused dehydration, as did HNO_3 in the attempt to obtain $\text{COPh}\cdot\text{CPhEt}\cdot\text{OH}$. Other oxidising agents are unsatisfactory, but when the glycol is dissolved in MgEtI and PhCHO in C_6H_6 is added, the *r*-ethylhydrobenzoin (α -form) gives *r*-ethylbenzoin, and *D*(+)-ethylhydrobenzoin (α -form)

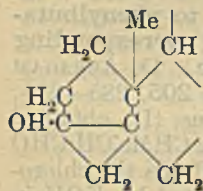
(I) gives (+)-ethylbenzoin (II), m.p. 71°, $[\alpha]_{5461}^{20} +252.7^\circ$ in EtOH, -182.4° in CS₂, $[\alpha]_{5791}^{20} -155.5^\circ$ in CS₂ (cf. this vol., 104). If no inversion of the mandelyl

complex occurs during the conversion of *D*(-)-mandelic acid (III) into (I), or during the dissolution of (I) in MgEtI, (I) has the annexed structure. Although (II) is the optical antipode of the (-)-ethylbenzoin from (+)- α -hydroxy- α -phenyl-*n*-butyric acid (IV) (*loc. cit.*), it is not possible to connect the configurations of (III) and (IV).

E. W. W.

Manufacture of *tert*-alkylaryloxyalkanols.—See B., 1937, 760.

Sterol group. XXXIII. Constitution of the isomeric ethers of cholesterol. J. H. BENYON, I. M. HEILBRON, and F. S. SPRING (J.C.S., 1937, 1459—1461; cf. this vol., 190, 344).—Cholesteryl *p*-toluenesulphonate and KOAc in 50% COMe₂ give *i*-cholesteryl acetate and thence *i*-cholesterol (I) in good yield; this with HCl-AcOH gives cholesteryl chloride, with Br-Et₂O gives tribromocholestane, and with K and MeI in C₆H₆ gives cholesterol Me “*iso*” ether. The relation of the *d*-ethers to (I) is thus proved. X-Ray examination proves the OH of (I) to be in position 3 and (I) is considered to contain the grouping shown.



R. S. C.

Molecular rearrangements in the sterols. II. Constitution of the isomeric ethers of cholesterol. E. G. FORD and E. S. WALLIS (J. Amer. Chem. Soc., 1937, 59, 1415—1416; cf. this vol., 99).—The so-called *cis*-cholesteryl ethers are *i*-cholesteryl ethers, probably formed by mol. rearrangement, since the K salt of *i*-cholesterol with MeI in C₆H₆ gives a Me ether, m.p. 78—78.5°, $[\alpha]_{579}^{20} +54^\circ$ in CHCl₃, identical with “*cis*-cholesteryl Me ether.” *epi*Cholesterol gives a Me ether, m.p. 88—89°, $[\alpha]_{579}^{20} -46.3^\circ$ in CHCl₃.

R. S. C.

Cholesterol derivatives. Y. URUSHIBARA, T. ANDO, H. ARAKI, and A. OZAWA (Bull. Chem. Soc. Japan, 1937, 12, 353—355).—Cholestenone with MgPhBr and α -C₁₀H₇·MgBr yields respectively 3-phenyl-, m.p. 174—175°, $[\alpha]_{579}^{20} -133^\circ$ in CHCl₃, and 3- α -naphthyl-cholestadiene, m.p. 131—133°, $[\alpha]_{579}^{20} -49.7^\circ$ in CHCl₃ (picrate, m.p. 161—163°). The intermediate OH-compound, unlike 7-hydroxy-7-phenylcholesterol (cf. Weinhouse and Kharasch, this vol., 192), could not be isolated. All m.p. are corr.

F. R. G.

X-Ray investigations of additive compounds of cholesterol. F. KLÖTZER (Z. Krist., 1937, 95, 338—367).—Unlike ergosterol, cholesterol (I) forms loose additive compounds with EtOH, MeOH, C₅H₅N, C₆H₆, and H₂O, which give distinctive powder diagrams. The monohydrate of (I) could be obtained in three forms when recryst. from EtOH-Et₂O solution. The normal form had *a* 12.82, *c* 12.25 Å., 16 mols. in unit cell. The structure of the other forms is discussed. From MeOH-Et₂O solution the compound, C₂₇H₄₅·OH·0.5MeOH, was obtained as triclinic

crystals (*a* 6.24, *c* 12.27 Å., 4 mols. in unit cell; space-group *C*₁ or *C*_i). Single crystals of (I) obtained from a melt had *a* 10.5, *c* 14.2 Å.; 8 mols. in unit cell; space-group *C*₁ or *C*_i. Contrary to the results of Bernal, who may have examined an additive compound (cf. A., 1932, 327, 658), the lattice of (I) is similar to that of ergosterol.

H. J. E.

Activation of cholesterol and cholesterolene.—See A., III, 364.

Sterols. XVI. Lanasterol and agnosterol. R. E. MARKER, E. L. WITTLE, and L. W. MIXON (J. Amer. Chem. Soc., 1937, 59, 1368—1373; cf. this vol., 424).—Lanosteryl acetate is reduced (PtO₂) to α -dihydro-, m.p. 119°, isomerised by HCl in CHCl₃ to β -dihydro-lanosteryl acetate, m.p. 149°. These two when hydrolysed give the dihydrolanosterols (α -, m.p. 148°, β -, m.p. 162°), oxidised by Cu (250° and 2 mm. pressure) to the stenones (α -, m.p. 122°, β -, m.p. 149°; 2:4-dinitrophenylhydrazones, α -, m.p. 213°, β -, m.p. 230°); the ketones when reduced (Na + Pr^{*n*}OH) yield the original sterols, which are therefore not epimeric. Lanosterol (I) and α -dihydrolanosterol (II) are dehydrogenated by Pt-black to the corresponding ketones (with no naphthol or PhOH), indicating the presence of an angular Me group. The acetates of (I) and (II) on vigorous oxidation (CrO₃) yield the same acid, C₂₅H₄₆O₂, m.p. 81° (Me ester, m.p. 67°), whilst that of (II) on mild oxidation (CrO₃) affords a mixture of α -, m.p. 150°, and β - (also produced on boiling α - with Ac₂O) -ketodihydrolanosteryl acetate, m.p. 152°, both hydrolysed to the same ketodihydrolanosterol, m.p. 134°, which with Ac₂O yields the β -acetate, and is reduced by Na + Pr^{*n*}OH to a hydroxy-dihydrolanosterol, m.p. 165°. Ac₂O converts this into a mixture of its acetate, m.p. 130°, and (removing one OH group) dihydroagnosteryl acetate, m.p. 169°, identical with that prepared from natural agnosterol.

A. LI.

Subsidiary sterols from yeast. V. Zymosterol and ascosterol. H. WIELAND and Y. KANAOKA [with, in part, W. E. BACHMANN] (Annalen, 1937, 530, 146—151; cf. this vol., 243).—Zymosterol (improved isolation), m.p. 126° (cloudy), 138° (clear) [formate, m.p. 75—76°; acetate, m.p. 105—106°; benzoate dibromide, m.p. 156—162° (decomp.); acetate dibromide, m.p. 176° (decomp.)], is shown to be C₂₇H₄₃·OH; the H₂-derivative, m.p. 120—121°, $[\alpha]_{579}^{20} +28.7^\circ$ in CHCl₃, with BzO₂H gives an oxide, m.p. 120° (decomp.). Ascosterol, m.p. 146—147°, $[\alpha]_{579}^{20} +45.1^\circ$ in CHCl₃ (benzoate, m.p. 135—136°, $[\alpha]_{579}^{20} +41.1^\circ$; acetate, m.p. 152—153°, $[\alpha]_{579}^{20} +21.5^\circ$ in CHCl₃), is shown to be C₂₇H₄₃·OH; it gives a H₂-derivative, m.p. 130—131° (acetate, m.p. 106—107°), which gives Liebermann's reaction and is yellow in C(NO₂)₄. Both these sterols thus contain two ethylenic linkages.

R. S. C.

Preparation of a homologue of epicoprosterol in the ergosterol series. F. WETTER and K. DEMROTH (Ber., 1937, 70, [B], 1665—1672).—Ergosteryl acetate-maleic anhydride is converted by gentle hydrolysis with NaOEt-EtOH at 50—60° into ergosterol-maleic acid, m.p. 120° (decomp.), $[\alpha]_{579}^{20} -46.3^\circ$ in MeOH (Me₂ ester, m.p. 72°), which when

heated rapidly to 120° and then slowly to 180° gives ergosterol-maleic anhydride, m.p. 202° (yield 80%), oxidised to *ergosterone-maleic acid*, m.p. 188°, which passes into ergoster-5-one-maleic anhydride. This at 220°/0.0005 mm. affords ergosterone (I), m.p. 132°, $[\alpha]_D^{20}$ -0.52° in CHCl_3 (cf. Oppenauer, this vol., 250) (*semicarbazone*, m.p. 251°, and an $\alpha\beta$ -unsaturated *ketone*, m.p. 183°. The mother-liquors from (I) yield *isoergosterone* (II), $\text{C}_{28}\text{H}_{42}\text{O}$, m.p. 110° (*semicarbazone*, m.p. 236°), which has a very marked tendency towards enolisation. (I) is isomerised to (II) by boiling HCl-MeOH . Hydrogenation of (I) proceeds similarly to that of cholestenone. In presence of Pd-black and EtOAc it absorbs 2 H_2 with formation of a non-cryst. product (II) (*semicarbazone*, $\text{C}_{28}\text{H}_{49}\text{ON}_3$, m.p. 238–239°), further hydrogenated (Pt-black in EtOAc) to a compound, $\text{C}_{28}\text{H}_{48}\text{O}$, m.p. 162° (*acetate*, m.p. 80°). Hydrogenation (PtO_2 in AcOH) of (II) followed by hydrolysis of the product and treatment of it with digitonin gives a ppt. from which *trans-ergostanol* is isolated, leaving a non-precipitable substance, $\text{C}_{28}\text{H}_{50}\text{O}$, m.p. 139–140°, $[\alpha]_D^{25}$ +24.8° in CHCl_3 (*acetate*, m.p. 99°), believed to be a homologue of *epicoprosterol*. H. W.

Introduction of double linkings into bile acids and sterols. II. Production of cholestadienol. E. DANE and Y. WANG (*Z. physiol. Chem.*, 1937, 248, I–III; cf. this vol., 61).—The dibromide (I) of cholesterol (II) when boiled with $\text{C}_5\text{H}_5\text{N}$ yields chiefly (II), but when AgNO_3 is added at room temp. to (I) in $\text{C}_5\text{H}_5\text{N}$ impure *cholestadienol* (probably $\Delta^{4,6}$), m.p. 115–121° (*digitonide*, m.p. 207–224°; *dinitrobenzoate*, m.p. 194°), is obtained. W. McC.

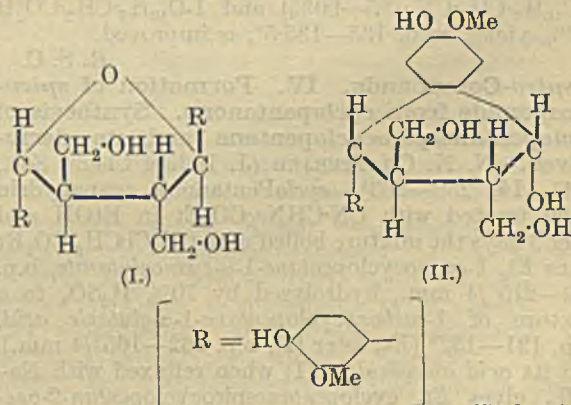
α - and β -Estradiol. A. BUTENANDT and C. GOERGENS (*Z. physiol. Chem.*, 1937, 248, 129–141; cf. Whitman *et al.*, this vol., 289).—Fractional crystallisation from EtOH of the 95:5 mixture of α -estradiols obtained by reduction of α -estrone with Ni-H_2 yields α -estradiol (I), m.p. 175–176°, $[\alpha]_D^{18}$ +78° in EtOH [3-*Me ether*, m.p. 97–98°; 3-*benzoate* (II), m.p. 192–193°; 3:17-*dibenzoate*, m.p. 168–169°; 3:17-*diacetate*, m.p. 125–126°], and β -estradiol (III), m.p. 216–218°, $[\alpha]_D^{18}$ +56.7° in EtOH [3-*Me ether*, m.p. 109–110°, 3-*benzoate* (IV), m.p. 150–151°, 3:17-*diacetate*, m.p. 139–140°]. (II) and (IV) in AcOH with CrO_3 at approx. 20° give α -estrone benzoate. (I) is pptd. by digitonin, but (III) is not. 1 g. of (I) contains 20×10^6 , 1 g. of (III) 0.6 – 0.8×10^6 , and 1 g. of (II) 13 – 15×10^6 mouse units. (I), which probably has the same configuration as has natural testosterone, differs from (III) only in the configuration of the groups attached to C_{17} . W. McC.

Steroids and related compounds. I. Isomeric cholestenediols. V. A. PETROW (*J.C.S.*, 1937, 1077–1081).—Attempts to prepare $\Delta^{4,6}$ -cholestadien-3-ol (I) from Δ^4 -cholestene-3:6-diol, or by dehalogenation of cholesteryl ester dibromides, are unsuccessful. Cholestane-3:5:6-triol diacetate (improved prep.) with H_2SO_4 in Ac_2O , followed by BzCl in $\text{C}_5\text{H}_5\text{N}$, gives 3:6-*dibenzoyloxy*- Δ^4 -cholestene, m.p. 163.5–164.5–182°, which is stable up to about 290°/5 mm., and then resinifies. The diacetate distils unchanged. Cholesteryl benzoate with H_2O_2 –

AcOH gives 5-*hydroxy*-3-*benzoyloxy*-6-*acetoxyste*chlestane, m.p. 162.5–163.5°, $[\alpha]_D$ -23.8° (all rotations in CHCl_3), which with H_2SO_4 in AcOH yields 3-*benzoyloxy*-6-*acetoxyste*- Δ^4 -cholestene, m.p. 138.5°; this decomposes above 280°/5 mm., but evolves BzOH , and does not give (I). Cholesteryl *Me ether* with H_2O_2 – AcOH forms a product hydrolysed to 5:6-*dihydroxy*-3-*methoxyste*chlestane, m.p. 154°, $[\alpha]_D$ -4.8° (6-*benzoyloxy*-compound, m.p. 96.5–97.5°, $[\alpha]_D$ -33.1°), of which the 6-*OAc*-compound, m.p. 118.5–119.5°, $[\alpha]_D$ -30.1°, is dehydrated by H_2SO_4 in Ac_2O to 6-*acetoxyste*-3-*methoxyste*- Δ^4 -cholestene, m.p. 121.5–122.5°, $[\alpha]_D$ +166.6°; this again distils unchanged. Cholesteryl acetate dibromide is dehalogenated by KOAc in abs. EtOH to cholesteryl acetate and *cis*-4-*hydroxy*-3-*acetoxyste*- Δ^5 -cholestene, m.p. 176–177°, $[\alpha]_D$ -84.4° [acetylated to *cis*-3:4-*diacetoxyste*- Δ^5 -cholestene (II), and hydrolysed to *cis*- Δ^5 -cholestene-3:4-diol (III)], and by AgNO_3 - $\text{C}_5\text{H}_5\text{N}$ to a product acetylated to (II). “Monobromocholesteryl bromide” is 5:5'-*dibromo*-3:3'-*dibenzoyloxy*-6:6'-*dicholestanyl*, which is dehalogenated (AgNO_3 - $\text{C}_5\text{H}_5\text{N}$) to (III). Cholesteryl benzoate dibromide with KOAc-EtOH or AgNO_3 - $\text{C}_5\text{H}_5\text{N}$ gives (II). E. W. W.

Sterol (“sapogenol”) from Shoyu oil. I. T. KAZUNO (*J. Biochem. Japan*, 1937, 25, 251–259).—The unsaponifiable fraction of the oil yields *sapogenol*, $\text{C}_{30}\text{H}_{50}\text{O}_3$, m.p. 258°, $[\alpha]_D^{21}$ +93.06° in CHCl_3 [*triacetate* (I), m.p. 178–179°; *tribenzoate*, m.p. 184–186°; *bromotriacetate* (II), decomp. 194°, which with AcOH-Zn gives an *isomeride* (III), m.p. 204°; *Br*-derivative, decomp. 310°, which on acetylation gives only (III) and is produced by hydrolysis of (II) or (III)]. Oxidation (CrO_3) of (I) under varying conditions yields a product, $\text{C}_{30}\text{H}_{45}\text{O}_4\text{Ac}_3$, m.p. 265–266°, a *diketone*, $\text{C}_{29}\text{H}_{44}\text{O}_2$, m.p. 250–251° (*dioxime*, m.p. 265–267°) [reduced (Clemmensen) to $\text{C}_{29}\text{H}_{48}$, m.p. 160°], and a monocarboxylic acid, $\text{C}_{30}\text{H}_{44}\text{O}_4$, m.p. 213° (*Me ester*, m.p. 174°). F. O. H.

Configuration of olivil and isoolivil. B. L. VANZETTI and P. DREYFUSS (*Atti R. Accad. Lincei*, 1937, [vi], 25, 133–136).—Synthesis and properties of olivil (I) and isoolivil (II) (cf. A., 1934, 1099; 1936, 842) and analogy with similar compounds indicate the spatial configurations shown.



F. O. H.

Preparation and properties of *N*-chloro-derivatives of *p*-sulphonamidobenzoic acid. I. ZILBERG

(Prom. Org. Chim., 1937, 3, 26—29).—Chlorination of aq. $p\text{-CO}_2\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ (I) at 55—60° yields the $N\text{-Cl-}$ (II) and $\text{-Cl}_2\text{-}$ derivative (III) of (I), the proportion of (III) increasing with time. The (III) content of the ppt. obtained by adding HCl or AcOH to the reaction mixture is inversely $\propto [\text{H}^+]$, and the same effect is obtained by adding acid to a solution of (II) in aq. Na_2CO_3 . The reaction $2(\text{II}) \rightarrow (\text{III}) + (\text{I})$ is postulated. R. T.

Some benzoylthiobenzamides. L. MUSAJO and V. AMORUSO (Gazzetta, 1937, 67, 301—306).—Arguments in favour of the $N\text{-Bz}$ structure for these compounds are reviewed. Thiobenzamide suspended in aq. NaHCO_3 gives with BzCl a red product, which on attempted purification gives Bz_2S_2 (?), and may contain an unstable $S\text{-benzoylthiobenzamide}$. Slightly modified methods for the prep. of $N\text{-methylthiobenzanilide}$, and of $S\text{-methyl-}$ and $S\text{-benzylthiobenzanilide}$, are described; $\text{SS'-ethylenebis(isothiobenzanilide)}$ has m.p. 75—76°. E. W. W.

Thio-acids. (MLLE.) F. BLOCH (Compt. rend., 1937, 204, 1342—1344; cf. A., 1903, i, 42).— MgPhBr with CS_2 in Et_2O containing I affords phenylcarbitronic acid, converted (SOCl_2) into the chloride (cf. A., 1921, i, 25), which is hydrolysed to thiobenzoic acid (I), an indistillable oil, the Na salt, m.p. 130°, of which with I gives Bz_2S_2 [also obtained from BzSH and I (cf. A., 1903, i, 418)], which indicates that a tautomeric form of (I) suffers oxidation. J. L. D.

Manufacture of di- and tri-iodo-derivatives of acylamino-acids and their salts.—See B., 1937, 841.

Effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1937, 12, 356—358).—The lowering by O_2 of the rate of reaction of Br with $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ in the dark (cf. Bauer and Daniels, A., 1934, 1216) has been studied quantitatively. No peroxide formation could be detected. F. R. G.

1-Naphthylacetic acid. S. C. J. OLIVIER and J. WIT (Rec. trav. chim., 1937, 56, 853—857).—The prep. of $1\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\text{Br}$ (32%) and thence of $1\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CN}$ (85—90%) and $1\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (92% yield), m.p. 135—135.5°, is improved. R. S. C.

spiro-Compounds. IV. Formation of spiro-compounds from cyclopentanone. Synthesis of cyclopentanespirocyclopentane and its derivatives. N. N. CHATTERJEE (J. Indian Chem. Soc., 1937, 14, 259—263).—*cyclopentanone* cyanohydrin when treated with $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ in EtOH and after 3 days the mixture boiled with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ gives Et_2 1-cyanocyclopentane-1- α -cyanoglutarate, b.p. 208—215°/4 mm., hydrolysed by 70% H_2SO_4 to a mixture of 1-carboxycyclopentane-1- α -glutaric acid, m.p. 131—132° [Et_3 ester (I), b.p. 162—165°/4 mm.], and its acid anhydride. (I) when refluxed with $\text{Na}\cdot\text{C}_6\text{H}_6$ gives Et_2 cyclopentanespirocyclopentane-2-one-3:5-dicarboxylate, b.p. 180—185°/4 mm., hydrolysed by 20% H_2SO_4 to cyclopentanespirocyclopentane-2-one-5-carboxylic acid (II), m.p. 67° (semicarbazone,

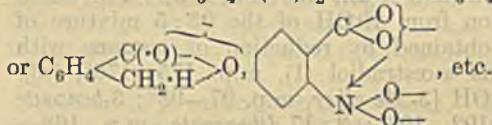
m.p. 232°; Et ester, b.p. 131—132°/4 mm.), reduced (Clemmensen) to an uncrystallisable acid, the Ca salt of which when heated with CaO gives cyclopentanespirocyclopentane, b.p. 60°/12 mm., in poor yield. This slowly decolorises KMnO_4 and is slightly less stable than the cyclohexane analogue. (II) when oxidised with conc. HNO_3 and then distilled gives cyclopentanecarboxylic acid. H. G. M.

Bromoalkyl derivatives of salicylic acid. E. MONESS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1937, 26, 618—620).—Attempts to prepare α -bromoacrylyl chloride from K α -bromoacrylate and SO_2Cl_2 or POCl_3 , and $\alpha\beta$ -dibromopropionyl-salicylic acid from salicylic acid and $\alpha\beta$ -dibromopropionyl chloride, yielded only resinous polymerisation products. Na salicylate with dibromopropene in COMe_2 gave bromoalkyl salicylate (I), b.p. 125—130°/1—2 mm. [impure Ac derivative (II) prepared]. (I) and (II) are superior to aspirin in antipyretic activity, but approx. 3 times as toxic. F. O. H.

Ortho-effect. I. Influence of substituents in the o-position on the chemical characters of carboxylic acids and their derivatives. J. F. J. DIPPEY, D. P. EVANS, J. J. GORDON, R. H. LEWIS, and H. B. WATSON (J.C.S., 1937, 1421—1425).—The regularities and irregularities of the effect of o -substituents are discussed. The effect is held to be due partly to steric hindrance, partly to H bond formation or chelation between o -substituents if one is polar, and partly to other causes. Structures are

postulated such as $\text{C}_6\text{H}_4\begin{array}{c} \text{C}(\text{O}) \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{O} \end{array}$, intermediate

between $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{O})\text{-}_2$ and $o\text{-O}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{O})\text{-OH}$,



R. S. C.

Benzylidenepyruvic acids. III. L. MUSAJO (Gazzetta, 1937, 67, 307—312).—Amorphous benzylidenepyruvic acid (II), from PhCHO (II) and AcCO_2H (III) (cf. A., 1933, 64), is a polymeride, $(\text{C}_{10}\text{H}_8\text{O}_3)_n$; from b.p. in AcOH, $n = 1$, and from f.p., $n = 2$ in AcOH or in PhOH, 3 in PhNO_2 . The Br-free acid, m.p. 279° (IV), obtained as a by-product from Br and (I) (cf. A., 1931, 221), best prepared in Et_2O , is converted by Br in AcOH or EtOH into a red or a yellow substance, respectively, both m.p. 210°, and both reconverted into (IV) when dissolved in alkali and acidified. (I) and (II) with NH_3 in EtOH yield 2-phenyl-4:5-diketotetrahydropyrrole (?), m.p. 215° (decomp.), and a substance, m.p. 230° (decomp.). E. W. W.

Syntheses in the carane group. I. Synthesis of 2:2-dimethylcycloheptane-1:3-dicarboxylic acid. P. C. GUHA and D. K. SANKARAN (Ber., 1937, 70, [B], 1683—1688).—Condensation of $\text{Br}[\text{CH}_2]_4\text{Br}$ with $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethylglutaramide and NaOMe in boiling MeOH gives a poor yield of 1:3-dicyano-2:2-dimethylcycloheptane-1:3-dicarboxylimide (I), m.p. 298°, the constitution of which

follows from the formation of an *Ag* salt and hydrolysis by H_2SO_4 to suberic acid. Boiling dil. alkali transforms (I) into 1:3-dicarbamyl-2:2-dimethylcycloheptane-1:3-dicarboxylic acid (II), m.p. 256°, and 1:3-dicyano-2:2-dimethylcycloheptane-1:3-dicarboxylic acid (III), m.p. 165–166°. Further treatment with alkali of (II) or (III) leads to 2:2-dimethylcycloheptane-1:1:3:3-tetracarboxylic acid, m.p. 173–174° (Et_4 ester, b.p. 110–115°/3 mm.), decarboxylated at 200–210° to 2:2-dimethylcycloheptane-1:3-dicarboxylic acid, m.p. 127–128° after softening at 112° (Et_2 ester, b.p. 138–140°/7 mm.). H. W.

Syntheses in the carane group. II. New synthesis of caronic and homocaronic acid. P. C. GUHA and D. K. SANKARAN (Ber., 1937, 70, [B], 1688–1691).— CMe_2N_2 (improved prep. from $\text{CMe}_2\text{N}\cdot\text{NH}_2$) condenses with Et_2 fumarate or maleate at –18° to the pyrazoline derivative,

$\text{N}-\text{CH}(\text{CO}_2\text{Et})-\text{CH}(\text{CO}_2\text{Et})-\text{CH}(\text{CO}_2\text{Et})-\text{CH}(\text{CO}_2\text{Et})-\text{N}$, which loses N_2 at 200–240° with production of Et_2 trans-caronate, b.p. 240–241°, hydrolysed by $\text{KOH}-\text{H}_2\text{O}$ to trans-caronic (1:1-dimethylcyclopropane-2:3-dicarboxylic acid (I), m.p. 213°. (I) is isomerised by Ac_2O at 220° to cis-caronic acid, m.p. 176°. Similarly CMe_2N_2 and Et_2 glutaconate give the pyrazoline compound, $\text{N}-\text{CH}(\text{CO}_2\text{Et})-\text{CH}(\text{CO}_2\text{Et})-\text{CH}(\text{CO}_2\text{Et})-\text{CH}(\text{CO}_2\text{Et})-\text{N}$, m.p. 152–153°, which gives successively Et_2 homocaronate, b.p. 253°, and trans-homocaronic [2:2-dimethylcyclopropane-1-carboxylic-3-acetic] acid, m.p. 191–192°, isomerised to the cis-acid, m.p. 135–136°. H. W.

$\alpha\alpha'$ -Dicyclohexylsuccinic acids. (Miss) A. R. MURRAY and T. W. J. TAYLOR (J.C.S., 1937, 1450–1453).—Many attempts to prepare $\alpha\alpha'$ -dicyclohexylsuccinic and $\alpha\beta$ -dicyclohexylpropionic acids by standard methods failed. $\text{Et H cyclohexylmalonate}$, m.p. 44–45°, best prepared from the Et_2 ester by KOH , boils at 163°/15 mm. with partial decomp. to $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$; electrolysis of the K salt gives Et_2 (?) meso-, m.p. 120°, and (?) dl- $\alpha\alpha'$ -dicyclohexylsuccinate, m.p. 60°. Hydrolysis of the former gives the (?) dl-, m.p. 147° (anhydride, m.p. 62–5°, gives the semianilide, m.p. 225°), and (?) meso-acid, m.p. 225°, +2 H_2O ; hydrolysis of the second ester gives the anhydride and the second acid. R. S. C.

Analogues of damascenine. I. Synthesis of methyl esters of dimethoxy-N-methylantranilic acids. V. M. RODIONOV and A. M. FEDOROVA (Bull. Acad. Sci. U.R.S.S., 1937, 501–509).—Hemipinimide is converted by the Hoffmann reaction into 3:4-(I) and 5:6-dimethoxyantranilic acid (II). The *Me* ester, m.p. 68–70°, of (I) with MeI in MeOH (110°; 5 hr.), or with *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ (III) (100°; 90 min.), affords *Me* 3:4-dimethoxy-N-methylantranilate, m.p. 110–112°. The *N*-benzylidene derivative, m.p. 148–150°, of (II) with MeOH in H_2SO_4 yields the *Me* ester, m.p. 49–51° (hydrochloride, m.p. 185–186°), of (II), which with (III) affords *Me* 5:6-dimethoxy-N-methylantranilate, m.p. 61–62° (hydrochloride, m.p. 171–172°). R. T.

β -Arylglutaconic acids. III. Condensations with phenolic ethers. G. R. GOGTE (Proc. Indian

Acad. Sci., 1937, 5, A, 535–542; cf. A., 1935, 1366).—Acetonedicarboxylic acid, from citric acid and conc. H_2SO_4 , diluted with H_2O reacts with PhOH at <0° to give coumarin-4-acetic acid (I), m.p. 184° [Limaye's product (cf. A., 1927, 974) when recrystallised has m.p. 184°], and $\beta\beta$ -4:4'-dihydroxydiphenylglutaric acid (II), m.p. 235° (decomp.) [Et_2 ester, m.p. 158–159°; Me_2 ester, m.p. 189°; Ac_2 derivative, m.p. 188–189° (decomp.) (Et_2 ester, m.p. 135°); Me_2 ether (III), m.p. 158°, which when heated affords the anhydride, m.p. 104–105°, converted by heating with NH_2Ph into the semianilide, m.p. 187°; anhydride, m.p. 204–205°], different from that obtained by Dixit and Gokhale (A., 1935, 353), as it gives no (I) with conc. H_2SO_4 and when heated gives no anhydride but loses CO_2 . β -*p*-Tolylglutaconic acid with PhOH and H_2SO_4 gives no analogue of (II), as the glutaconic acid is decomposed by H_2SO_4 . β -*p*-Anisylglutaconic acid (IV) with PhOMe and 75% aq. H_2SO_4 at room temp. affords (III), which with warm 80% H_2SO_4 is converted into (IV). β -*o*-Anisylglutaconic acid does not condense with PhOMe . Hot dil. acids have no effect on (III), but when heated with CaO it affords *as*-di-*p*-anisylethylene, which establishes the structure of (II). A $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2-\text{H}_2\text{SO}_4$ mixture with PhOMe at 0° affords (III). $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ and PhOEt yield β -*p*-phenetylglutaconic acid, m.p. 170° (decomp.) [hydroxyanhydride, m.p. 178°; semianilide, m.p. 180° (decomp.)], which with PhOEt , or by ethylating (II), gives $\beta\beta$ -di-*p*-phenetylglutaric acid, m.p. 157–158° (anhydride, m.p. 119–120°), which when heated with CaO gives *as*-di-*p*-phenylethylene. β -6-Methoxy-*m*-tolylglutaconic acid (V) or $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ with *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$ in 80% H_2SO_4 at 0° affords $\beta\beta$ -di-(6-methoxy-*m*-tolyl)glutaric acid, m.p. 187° (*Ba* salt; anhydride, m.p. 156°; semianilide, m.p. 189°), converted by warm 80% H_2SO_4 into (V) (cf. A., 1932, 512) and by heating with CaO into *as*-di-(6-methoxy-*m*-tolyl)ethylene, m.p. 106°. β -6-Ethoxy-*m*-tolylglutaconic acid, m.p. 174° (decomp.) (hydroxyanhydride, m.p. 188°; semianilide, m.p. 173°), or $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ with *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OEt}$ gives $\beta\beta$ -di-(6-ethoxy-*m*-tolyl)glutaric acid, m.p. 204° (decomp.) (*Ba* salt; anhydride, m.p. 104–105°; semianilide, m.p. 155–156°), converted when heated with CaO into *as*-di-(6-ethoxy-*m*-tolyl)ethylene, m.p. 95–96°.

J. L. D.

Formation of dopa [l-3:4-dihydroxyphenylalanine] by exposure of tyrosine solutions to ultra-violet radiation. L. E. ARNOW (J. Biol. Chem., 1937, 120, 151–153).—Ultra-violet irradiation of tyrosine (I) solutions results in destruction of (I) and formation of l-3:4-dihydroxyphenylalanine, which is also destroyed by ultra-violet irradiation. J. L. C.

Thyroxine from quinol monomethyl ether and 3:4:5-tri-iodonitrobenzene. A. J. SAVITZKI (Med. exp., Ukraine, 1934, No. 1, 39–49).—A modified synthesis is described. It is possible to avoid etherification and obtain α -amino- β -(3:5-di-iodo-4:4'-hydroxyphenoxyphenyl)propionic acid directly; this is then iodinated to thyroxine in good yield. CH. ABS. (r)

Synthesis of compounds related to the sterols, bile acids, and oestrus-producing hormones.

XI. A "diene-synthesis" of phenanthrene and hydrophenanthrene derivatives. A. COHEN and (in part) F. L. WARREN (J.C.S., 1937, 1315—1320).—An extension and correction of previous work (cf. A., 1936, 71). 1-Vinylnaphthalene and maleic anhydride in xylene give, not dihydro- (*loc. cit.*), but homogeneous 1:2:3:11-tetrahydro-phenanthrene-1:2-dicarboxylic anhydride (I), m.p. 186—189°, unsaturated to KMnO_4 or to BzO_2H , which is converted by boiling AcOH-HCl into saturated 1:2:3:4-tetrahydrophenanthrene-1:2-dicarboxylic anhydride (II), m.p. 220°. Either (I) with $\text{NaOH-Me}_2\text{SO}_4$ or (II) with MeOH-HCl gives the Me_2 ester (III), m.p. 105—106°, of the acid from (II). Dehydrogenation of (I) or (II) gives phenanthrene-1:2-dicarboxylic anhydride (IV). With MeMgI , (II) forms (III) and the dimethyl-lactone (V), m.p. 213.5—214.5° (*K* salt of the OH-acid), with a keto-ester (?), b.p. 185—190°/0.2 mm. With Na in EtOAc , followed by 5*N*-HCl at 100°, (II) gives only 1':3'-diketocyclopentenophenanthrene. Hydrogenation of (I) gives a mixture containing (II). 6-Methoxy-1-vinylnaphthalene gives (cf. *loc. cit.*) 7-methoxy-1:2:3:11-tetrahydrophenanthrene-1:2-dicarboxylic anhydride, m.p. 171—175°, unsaturated to KMnO_4 , dehydrogenated (Pt at 280°) to 7-methoxyphenanthrene-1:2-dicarboxylic anhydride (VI). 2-Vinylnaphthalene gives 2:3:4:12-tetrahydrophenanthrene-3:4-dicarboxylic anhydride, m.p. 170—180°, dehydrogenated to phenanthrene-3:4-dicarboxylic anhydride.

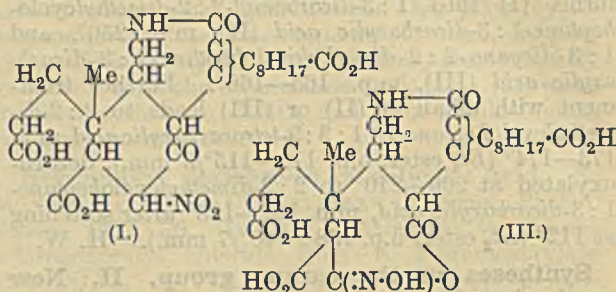
No oestrogenic activity is detected in (I), (II), (IV), (V), or (VI), or in the 3:4- H_2 -derivatives of (VI) or of the corresponding 7-OH-compound. E. W. W.

3-Hydroxy-6-ketoallocholanolic acid and synthesis of α :3:6-dihydroxyallocholanolic acid. G. SUGIYAMA (J. Biochem. Japan, 1937, 25, 157—165).—3-Hydroxy-6-ketoallocholanolic acid (Fernholz, A., 1935, 773), isolated from bile as the *Ac* derivative, m.p. 210—212°, is hydrogenated to α :3:6-dihydroxyallocholanolic acid (I), m.p. 247°, $[\alpha]_D^{25} +9.36^\circ$ in EtOH . The differentiation of (I) from Wieland's $(\text{OH})_2$ -acid (A., 1926, 723) is discussed. F. O. H.

Toad bile. VI. Constitution of trihydroxy-isosterocholenic acid. T. SHIMIZU and T. KAZUNO (J. Biochem. Japan, 1937, 25, 245—249; cf. A., 1936, 469).—*Me* isosterocholenate, converted into ozonide and treated successively with H_2O , *N*-NaOH, and dil. HCl, yields a bisnorcholanolic acid, m.p. 208—210°; similar treatment of *Me* trihydroxyisosterocholenate (I) affords bisnorcholic acid. Hence (I) has the double linking between $\text{C}_{(22)}$ and $\text{C}_{(23)}$ and the three OH at $\text{C}_{(3)}$, $\text{C}_{(7)}$, and $\text{C}_{(12)}$. F. O. H.

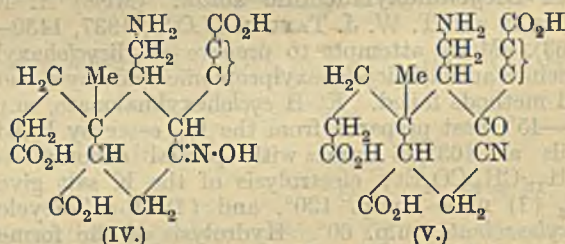
Bile acids. LII. (A) Constitution of the " β -acid" $\text{C}_{24}\text{H}_{34}\text{O}_{10}\text{N}_2$ and the compound $\text{C}_{24}\text{H}_{36}\text{O}_{11}\text{N}_2$ obtained from the " α -acid" by addition of water. (B) Determination of nitrogen according to Van Slyke. (C) Constitution of the "oxidation product," $\text{C}_{24}\text{H}_{36}\text{O}_9\text{N}_2$. M. SCHENK (Z. physiol. Chem., 1937, 248, 174—182; cf. this vol., 246).—(A) The α -acid (I) is converted by short treatment with boiling 10% HCl into the "nitroamino-acid" (II), $\text{C}_{24}\text{H}_{36}\text{O}_{11}\text{N}_2$, and by 90% H_2SO_4 at 100° into the " β -acid" (III), which does not afford a product analogous to (II). (I) and (III) behave as tetrabasic acids. (I) in EtOH gives with FeCl_3 a

reddish-yellow liquid from which a pale ppt. separates, whereas (III) under similar conditions gives an intense



brownish-red colour or ppt. The possibility that the change represents a simple tautomerisation is discounted by the apparent impossibility of transforming (III) into (I). (III) when boiled with acid and then rendered alkaline gives a solution which reduces cold Fehling's solution and $\text{Ag}_2\text{O-NH}_3$ probably owing to elimination of NH_3OH . (II) gives a pale brown colour with Fehling's solution. In (II) the NO_2 -CO grouping appears more stable than in (I). (I), (II), and (III) give NH_3 when boiled with acids and evolve N_2 by Van Slyke's method.

(B) Results of Van Slyke determinations can be used only with great caution if at all in elucidating the constitution of the bile acids. (I) gives 92% and the analogously-constituted nitrobilianic acid only 55% of the calc. amount of N_2 . Bilianic acid does not yield N_2 , but its oxime-lactam and dioxime evolve large amounts of gas which may not be exclusively N_2 . The acid (IV) gives very high N vals.; it appears



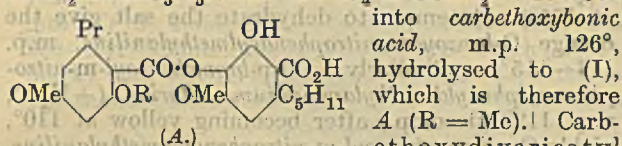
probable that the "by-product B" obtained by the action of 90% H_2SO_4 on (IV) (*loc. cit.*) is unchanged (IV).

(c) The "oxidation product," obtained from (IV) and alkaline KMnO_4 , after prolonged boiling with HCl does not reduce Fehling's solution or $\text{Ag}_2\text{O-NH}_3$ after addition of alkali. NH_3 is formed; it is probably (V), although the presence of CO could not be established by oximation. H. W.

β -Hyodeoxycholic acid from pig's bile.—See A., III, 377.

Lichen substances. LXXXIII. New depside, bonic acid; synthesis of bonic acid and of homosekikaic acid. Y. ASAHINA and T. KUSAKA (Ber., 1937, 70, [B], 1815—1821).—Percolation of the thalli of *Ramalina boninensis*, Y. Asahina, with Et_2O and treatment of the dried extract with C_6H_6 gives *d*-usnic acid and bonic acid (I), $\text{C}_{25}\text{H}_{32}\text{O}_8$, m.p. 134.5° [*Me* ester (II), m.p. 86°], converted by excess of CH_3N_2 in COMe_2 into *Me* ramalinolate Me_3 ether, m.p. 74—

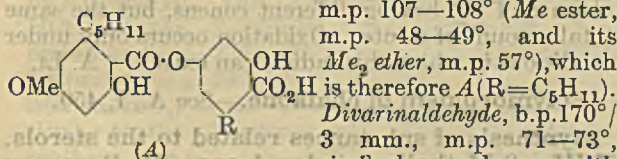
75°. Hydrolysis of (I) by conc. H_2SO_4 at 0° affords 2:3-dihydroxy-4-methoxy-6-n-amybenzoic acid (III), m.p. 143—144°, and divaricatic acid Me ether, m.p. 64°, whilst the latter substance and Me 2:3-dihydroxy-4-methoxy-6-n-amybenzoate (IV), m.p. 74°, are obtained similarly from (II). 3-Hydroxy-2:4-dimethoxy-6-n-amybenzaldehyde is converted into the corresponding *anil*, which is demethylated by $\text{NH}_2\text{Ph}\cdot\text{HI}$ to 2:3-dihydroxy-4-methoxy-6-n-amybenzylideneaniline, m.p. 101°; this is hydrolysed to 2:3-dihydroxy-4-methoxy-6-n-amybenzaldehyde (+ H_2O) (V), m.p. 68—69°, which is treated with ClCO_2Et in $\text{C}_5\text{H}_5\text{N}$ and then oxidised by KMnO_4 in COMe_2 to 4-methoxy-2:3-dicarbethoxy-6-n-amybenzoic acid, m.p. 101°; this is transformed by $2\text{N}\cdot\text{NH}_3$ at 20° into (III), whereas the corresponding Me ester, m.p. 43—44°, is converted by cautious treatment with KOH at 18° into (IV). (V) and divaricatyl chloride Me ether in $\text{C}_5\text{H}_5\text{N}$ at room temp. give *bonaldehyde*, m.p. 105—106°, converted by successive action of ClCO_2Et in $\text{C}_5\text{H}_5\text{N}$ and KMnO_4 in COMe_2 at 40—50°



into carbethoxybenzoic acid, m.p. 126°, hydrolysed to (I), which is therefore A (R = Me). Carbethoxydivaricatyl chloride and (V) in $\text{Et}_2\text{O}\text{--}\text{C}_5\text{H}_5\text{N}$ give non-cryst. carbethoxyhomosekikaldehyde (hydrazone, m.p. 186—187°), transformed by ClCO_2Et followed by oxidation into dicarbethoxyhomosekikaic acid, m.p. 101°, whence homosekikaic acid, m.p. 133—134° (Me ester, m.p. 106°), which is therefore A (R = H). H. W.

Lichen substances. LXXXIV. Occurrence of homosekikaic acid in *Cladonia*. Y. ASAHINA and T. KUSAKA [with, in part, T. SASAKI] (Ber., 1937, 70, [B], 1821—1823).—Homosekikaic acid (I) is obtained from Japanese *C. subpityrea*, Sandst., but not from the European lichen. With fumarprotocetraric acid (I) is isolated from *C. pityrea*, Flk., *f. phyllophora*, Mudd. H. W.

Lichen substances. LXXXV. Synthesis of perlatolic and imbricatic acid. Y. ASAHINA and I. YOSIOKA (Ber., 1937, 70, [B], 1823—1826).—4-Methoxy-2-carbethoxy-6-n-amybenzoyl chloride (I), from the corresponding acid, m.p. 72—73°, and SOCl_2 , condenses with 2:4-dihydroxy-6-n-amybenzaldehyde in Et_2O to the non-cryst. carbethoxyperlatolaldehyde (p-nitrophenylhydrazone, m.p. 176—178°), which is converted by ClCO_2Et in $\text{C}_5\text{H}_5\text{N}$ at —15° followed by KMnO_4 in COMe_2 into dicarbethoxyperlatolic acid, m.p. 83—84°, whence perlatolic acid, m.p. 107—108° (Me ester, m.p. 48—49°, and its Me₂ ether, m.p. 57°), which is therefore A (R = C_5H_{11}). Divarinaldehyde, b.p. 170°/3 mm., m.p. 71—73°, similarly condenses with (I) to the non-cryst. carbethoxyimbricaraldehyde (p-nitrophenylhydrazone, m.p. 163°), whence dicarbethoxyimbricatic acid, m.p. 102—103°, and imbricatic acid, m.p. 122° (Me ester Me₂ ether, m.p. 86—87.5°), which hence is A (R = Pr). H. W.



Lichen substances. LXXXVI. Synthesis of divaricatic and anziaic acid. Y. ASAHINA and M. HIRAIWA (Ber., 1937, 70, [B], 1826—1828).—Dicarbethoxydivarinaldehyde is oxidised by KMnO_4 in $\text{H}_2\text{O}\text{--}\text{COMe}_2$ at 40° to dicarbethoxydivaric acid, m.p. 81°, transformed successively into divaric acid, its Me ester, and divaricatinic acid. Carbethoxydivaricatinic acid is converted into the corresponding chloride, which condenses with divarinaldehyde in $\text{C}_5\text{H}_5\text{N}$ at —15° to dicarbethoxydivaricataldehyde, which is further carbethoxylated and then oxidised to dicarbethoxydivaricatic acid, m.p. 101°, whence divaricatic acid identical with the natural substance. Dicarbethoxyolivetolcarboxylic acid, m.p. 62—63°, is converted into the chloride, which when treated successively with olivetolaldehyde in $\text{C}_5\text{H}_5\text{N}$ and ClCO_2Et in Et_2O gives tricarbethoxyanzia-aldehyde, an oil, which is oxidised by KMnO_4 and MgSO_4 at 40° to tricarbethoxyanziaic acid, m.p. 108°; this is hydrolysed to anziaic acid, identical with the product from natural sources. H. W.

Cannizzaro reaction. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1937, 12, 328—329).—Evidence is given showing that the Cannizzaro reaction may be regarded as a chain reaction, in which the peroxide of the aldehyde is actively concerned. The reaction is not catalysed by ferro-magnetic metals. F. N. W.

Hydrolysis of N-substituted benzaldoximes. P. GRAMMATICAKIS (Compt. rend., 1937, 205, 60—62).—N-Benzylbenzaldoxime with MgEtBr gives benzyl- α -phenylpropylhydroxylamine, m.p. 99° (hydrochloride, m.p. 180°; Ph carbamate, m.p. 155°), oxidised to benzylidene- α -phenylpropylamine oxide, m.p. 116°, hydrolysed (HCl) to α -phenylpropylhydroxylamine, m.p. 75° (hydrochloride, m.p. 135°), and PhCHO. Similarly prepared, benzylidene- α -p-tolylpropylamine oxide and α -p-tolylpropylhydroxylamine have m.p. 112° and 82° (hydrochloride, m.p. 132°), respectively; N-benzyl-N- α -p-anisylpropylhydroxylamine, m.p. 78°, is oxidised to benzylidene- α -p-anisylpropylamine oxide, m.p. 88° and 97°, hydrolysed to PhCHO, NH_2OH , and α -p-anisylpropyl alcohol, which loses H_2O to give α -p-anisyl- Δ^2 -propene. N-Benzyl-p-anisalaldoxime with MgPhBr or N-benzylbenzaldoxime with $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$ affords N-benzyl-N- α -p-anisylbenzylhydroxylamine, m.p. 108° (hydrochloride, m.p. 190°), oxidised to benzylidene- α -p-anisylbenzylamine oxide, m.p. 160°, identical with the product obtained from the Na derivative of p-methoxybenzophenone-oxime and CH_2PhCl , and from which N is eliminated by hydrolysis. J. L. D.

Catalytic hydrogenation of cinnamaldehyde and citronellal. M. DELÉPINE and C. HANEGRAEFF (Compt. rend., 1937, 205, 185—188).— $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ (I) and citronellal (II) in EtOH (sometimes containing NaOH) with H_2 -Raney Ni afford products, the extent of reduction being assessed from the I val. and the amount of $\cdot\text{CHO}$ present. Ni-Pt is a better catalyst in the reduction of (I) and if, in addition, 10N-NaOH is added after 1 hr. (when most of the reduction is accomplished), the reaction is completed in 1 hr. more as against a total of 4 hr. without NaOH and 8 hr. without Pt or NaOH.

The product is $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$. In the total reduction of (II), neither NaOH nor Pt has much accelerating influence. Reductions carried out for shorter periods show that in (I) the double linking is reduced more readily than $\cdot\text{CHO}$, whereas in (II) $\cdot\text{CHO}$ is rapidly reduced and the double linking but slowly. In the reaction with (II), NaOH plays a part in the reduction. J. L. D.

Chloromethylation of anisaldehyde. Conversion into 4-methoxy-3-hydroxymethylbenzaldehyde. R. QUELET and J. ALLARD (Compt. rend., 1937, 205, 238—240; cf. A., 1901, i, 726).— $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (2 mol.), 40% CH_2O , and ZnCl_2 with HCl (gas) at 90° afford 4-methoxy-3-chloromethylbenzaldehyde (I), m.p. 60° (semicarbazone, m.p. $192\text{—}193^\circ$), oxidised (warm 5% KMnO_4) to 4-methoxyisophthalic acid, m.p. $273\text{—}275^\circ$. When crude (I) is boiled with aq. K_2CO_3 it affords 4-methoxy-3-hydroxymethylbenzaldehyde, m.p. 50° (phenylurethane, m.p. 103°). (I) with NaOMe and NaOEt affords, respectively, 4-methoxy-3-methoxymethyl-, m.p. 35° (semicarbazone, m.p. 150°), and 3-ethoxymethylbenzaldehyde, b.p. $173\text{—}175^\circ/15\text{ mm.}$ (semicarbazone, m.p. 141°). J. L. D.

Manufacture of benzaldehydes containing trifluoromethyl groups.—See B., 1937, 761.

Action of magnesium methyl bromide on 2:4:6-trichlorobenzoyl chloride. W. E. ROSS and R. C. FUSON (J. Amer. Chem. Soc., 1937, 59, 1508—1510).—Addition of 2:4:6- $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{COCl}$ (I) to 10 mols. of MgMeI gives 2:4:6-trichloroacetophenone (II), m.p. 51° (benzylidene derivative, m.p. $100\text{—}101^\circ$); use of 1—2 mols. of MgMeI leads, however, to di-2:4:6-trichlorobenzoylmethane (II), m.p. $160\text{—}161^\circ$ (red FeCl_3 colour; Cu derivative; gives 2CH_4 with MgMeI , only 1 mol. being liberated rapidly), also obtained by heating (II) with MgMeI and then adding (I), and previously (A., 1933, 66) considered to be (I). NaOBr converts (I) into 2:4:6-trichloro- $\alpha\alpha\alpha$ -tribromoacetophenone, m.p. $77\text{—}78^\circ$, stable to hot 40% aq. NaOH , but decomposed by hot 20% $\text{NaOH}\text{—EtOH}$ (no $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{CO}_2\text{H}$ was obtained). NaOCl gives $\alpha\alpha\alpha$ -2:4:6-hexachloroacetophenone, b.p. $127\text{—}128^\circ/1.5\text{ mm.}$, cleaved by NaOH (20 g.) in 10% aq. EtOH (100 c.c.) to $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{CO}_2\text{H}$. $\text{Cl}_2\text{—AcOH}$ or aq. NaOCl converts (II) into dichlorodi-2:4:6-trichlorobenzoylmethane, m.p. $106\text{—}108^\circ$; dibromodi-2:4:6-trichlorobenzoylmethane, m.p. $135\text{—}136^\circ$, is obtained by analogous methods. R. S. C.

Enol betaines. VI. Enol betaines without pyridine ring. F. KRÖHNKE and W. HEFFE (Ber., 1937, 70, [B], 1720—1727).— m -Nitrophenacyl bromide and NPhMe_2 give m -nitrophenacylphenyldimethylammonium bromide, m.p. 154° (decomp.) (corresponding perchlorate, m.p. 192° , sulphate, m.p. 227° , and chloride, m.p. $132\text{—}133^\circ$), converted by N-NaOH in presence of Et_2O into the orange-coloured betaine (I), $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}^-\cdot\text{CH}^+\cdot\text{N}^+\text{PhMe}_2$ ($+0.33\text{H}_2\text{O}$), m.p. $74\text{—}75^\circ$. The action of alkali on p -bromophenacylphenyldimethylammonium bromide, m.p. 153° (corresponding sulphate, m.p. 183°), or 3:4-dichlorophenacylphenyldimethylammonium bromide, m.p. 141.5° , gives colourless hydrates of bases which lose $1\text{H}_2\text{O}$ when dried, giving the colourless enol betaines (II), m.p.

119° (decomp.), and (III), m.p. $115\text{—}116^\circ$ (slight decomp.), re-convertible into the salts. Their reactions resemble those of (I) so closely that the structures must be identical. Since (II) and (III) give orange solutions in PhNO_2 , doubtless owing to the formation of an additive compound, it appears that in (I) there is a subsidiary valency relationship between the two N atoms. The new bases do not give a colour with chloranil and only a somewhat subdued colour with picryl chloride. Generally CH in them is much less reactive than in the pyridinium-methine enol betaines. Thus $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ and (II) give the expected keto-nitrone slowly at 50° whereas in the $\text{C}_6\text{H}_5\text{N}$ series the change is instantaneous at 0° . The diminished reactivity of CH is also shown by the formation of O -derivatives with acyl chlorides. Thus (I) and BzCl in CHCl_3 afford O -benzoyl- m -nitrophenacylphenyldimethylammonium chloride ($+1\text{H}_2\text{O}$), m.p. 128° after becoming yellow at 90° (greatly dependent on the mode of heating) (corresponding sulphate, m.p. $178\text{—}179^\circ$ after softening and becoming green at 155°). Attempts to dehydrate the salt give the orange O -benzoyl- m -nitrophenacylmethylaniline, m.p. $114\text{—}115^\circ$. Similarly, O - p -bromobenzoyl- m -nitrophenacylphenyldimethylammonium chloride ($+1\text{H}_2\text{O}$), m.p. 112° (decomp.) after becoming yellow at 110° , yields O - p -bromobenzoyl- m -nitrophenacylmethylaniline, m.p. 119° . Analogously, O -benzoyl- p -bromophenacylphenyldimethylammonium chloride, m.p. 117° [corresponding sulphate ($+1\text{H}_2\text{O}$), m.p. (anhyd.) 171° , and bromide, m.p. 115°], affords O -benzoyl- p -bromophenacylmethylaniline, m.p. 131° . O - m -Nitrobenzoyl- p -bromophenacylphenyldimethylammonium chloride, m.p. 135° (decomp.), gives an orange resin when heated. The possible activity of the enol O in pyridinium enol betaines is established by the conversion of dibenzoylmethylpyridinium enol betaine by BzCl in CHCl_3 into O -benzoyldibenzoylmethylpyridinium chloride ($+3\text{H}_2\text{O}$), m.p. 105° (corresponding picrate, perchlorate, iodide, bromide, sulphate, chromate, nitrate, and oxalate). 3-Nitro-4-methylphenacylphenyldimethylammonium bromide, m.p. 131° , gives the corresponding enol betaine, trihydrate, m.p. 86° , semihydrate, m.p. 116° .

Reply is made to Gustafsson (this vol., 386).

H. W.

Two-step oxidation of benzoin to benzil. L. MICHAELIS and E. S. FETCHER (J. Amer. Chem. Soc., 1937, 59, 1246—1249).—The purple colour in the oxidation of benzoin is due to a unimol. radical, $\text{COPh}\cdot\dot{\text{C}}\text{Ph}\cdot\text{OH}$ (and not a bimol. compound), since the total colour is (very nearly) the same in columns of solution (benzoin and benzil in $\text{NaOH}\text{—EtOH}$, in absence of O_2) having different concns. but the same total amount of solute. Oxidation occurs only under conditions in which this radical can exist. A. LI.

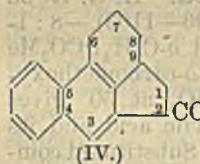
Polymorphism of chalkone.—See A., I, 450.

Synthesis of substances related to the sterols. XVII. 8-Methylhydrindan-1-one. R. ROBINSON and J. WALKER (J.C.S., 1937, 1160—1161).—The impure hydrogenation product of the unsaturated compound from Et 2-methyl-1- γ -methoxypropylcyclohexan-1-ol-2-carboxylate (this vol., 197) is purified by heating with KHSO_4 and renewed hydrogenation

(Pd-SrCO₃) to *Et* 2-methyl-1- γ -methoxypropylcyclohexane-2-carboxylate, b.p. 138—140°/12 mm., which with HBr-Ac₂O followed by KOAc-AcOH and 2.5% KOH-MeOH gives *Et* 2-methyl-1- γ -hydroxypropylcyclohexane-2-carboxylate, b.p. 160—165°/13 mm. This is converted after hydrolysis [Ba(OH)₂-MeOH and KOH-EtOH] by oxidation with KMnO₄ into 2-methylcyclohexane-2-carboxylic-1- β -propionic acid, cyclised to 8-methylhydrindan-1-one (cf. this vol., 343).

E. W. W.

Substances with a female hormone effect.
Synthesis of 4:5-benzo-6:7:8:9-tetrahydroacacenaphthen-2-one. J. HOSH (Compt. rend., 1937, 205, 65—67).—CHNa(CO₂Et)₂ with β -1-naphthylethyl bromide affords *Et*₂ β -1-naphthylethylmalonate, b.p. 200—202°/2 mm., hydrolysed (EtOH-KOH) to β -1-naphthylethylmalonic acid, m.p. 159°, which by loss of CO₂ gives γ -1-naphthylbutyric acid (I), m.p. 107—108°. (I) is cyclised by SnCl₄ to 1-keto-1:2:3:4-tetrahydrophenanthrene, m.p. 98°, converted by CH₂Br-CO₂Et in presence of Zn in C₆H₆ into *Et* 3:4-dihydro-1-phenanthrylacacetate (II), b.p. 238—241°/12 mm., the H₂-derivative of which (H₂-Pt-black) with EtOH-KOH gives 1:2:3:4-tetrahydro-1-phenanthrylacetic acid (III), m.p. 134°, the chloride of which is cyclised (AlCl₃ in C₆H₆ at 0°) to 4:5-benzo-6:7:8:9-tetrahydroacacenaphthen-2-one (IV), m.p. 112° (semicarbazone, m.p. 240—242°). 3:4-Dihydro-1-phenanthrylacetic acid, m.p. 147°, obtained by hydrolysing (II), when heated with



S at 180—200° affords 1-phenanthrylacetic acid, m.p. 189—190°, and some 1-methylphenanthrene, m.p. 119° (picrate, m.p. 135°).

J. L. D.

Phenanthrene series. XV. Substitution in 9:10-dihydrophenanthrene: tetracyclic compounds derived from it. A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1937, 59, 1302—1307).—The oxime of 2-acetyl-9:10-dihydrophenanthrene is converted by HCl and Ac₂O in glacial AcOH into 2-acetamido-, m.p. 173—174°, hydrolysed to 2-amino-9:10-dihydrophenanthrene (oily) [hydrochloride, m.p. 323—325° (decomp.) in vac.; picrate, m.p. 203° (decomp.)]; the 2-propionamido-derivative, m.p. 109—110°, is obtained similarly. Methylation (Me₂SO₄) of the amine gives a methiodide which when heated yields 2-dimethylamino-, m.p. 65—66° (hydrochloride, m.p. 186—188°), and diazotisation followed by boiling yields 2-hydroxy-9:10-dihydrophenanthrene, m.p. 111.5—113° (2-OMe- and -OAc-derivatives, oily). 9:10-Dihydrophenanthrene (I) is converted by HCl and HCN (AlCl₃) followed by decomp. with dil. HCl into the -2-aldehyde, b.p. 185°/2 mm. [semicarbazone, m.p. 235—236° (decomp.)]; p-nitrophenylhydrazones, m.p. 242—244° (decomp.)], which is oxidised (KMnO₄) to the -2-carboxylic acid, and reduced (PtO₂) to the -2-carbinol, m.p. 77—78° (α -naphthylurethane, m.p. 145—146°). 1:2-Benzanthracene (characterised by its picrate and quinone) is prepared from (I) by condensation (AlCl₃ in PhNO₂) with (·CH₂·CO)₂O giving β -2-(9:10-dihydrophenanthroyl)-propionic acid, m.p. 157.5—158.5° [also obtained by condensing (Na) the 2-bromoacetyl compound with

CH₂(CO₂Et)₂]; this is reduced (Zn-Hg) to γ -2-(9:10-dihydrophenanthroyl)butyric acid, m.p. 92°, cyclised with 85% H₂SO₄ to 8-keto-3:4:5:6:7:8-hexahydro-1:2-benzanthracene, m.p. 97—98° (oxime, m.p. 197—198°); the semicarbazone, m.p. 277—279° (decomp., in vac.), of this is reduced (Na, EtOH) and the product dehydrogenated with Se at 300°. cycloPenteno-phenanthrenes are prepared from the -2-aldehyde of (I) by condensation with CH₂(CO₂H)₂ (in C₅H₅N) to β -2-(9:10-dihydrophenanthroyl)acrylic acid, m.p. 153—154°; cyclisation (PCl₅ in C₆H₆, then AlCl₃) gives a mixture of 1'- (20%), m.p. 143—144° [semicarbazone, m.p. 263—268° (decomp., in vac.)], and 3'-keto-9:10-dihydro-2:3-cyclopentenophenanthrene (80%), m.p. 131—132° [semicarbazone, m.p. 261—263° (decomp., in vac.); oxime, m.p. 243—245° (decomp.)]; reduction (Zn-Hg) followed by dehydrogenation of these two gives 1:2- and 2:3-cyclopentenophenanthrene, m.p. 84—84.5° (picrate, m.p. 156—157°; styphnate, m.p. 158—159°).

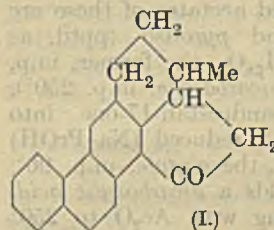
A. LI.

Synthesis of 2:3-cyclopentenophenanthrene. E. BERGMANN and O. BLUM-BERGMANN (J. Amer. Chem. Soc., 1937, 59, 1572—1573).—cycloPentane-1:2-dicarboxylic anhydride and 1-C₁₀H₇MgBr in Et₂O give 2-1'-naphthoylecyclopentancarboxylic acid, +1.5H₂O, converted by crystallisation from MeOH into the hydroxy-lactone form, anhyd., m.p. 169—170° after sintering, and reduced (Clemmensen) to 2-1'-naphthylmethylcyclopentanecarboxylic acid, m.p. 99—101°, which with SnCl₄ in PhMe or, better, P₂O₅ in C₆H₆ (H₂SO₄ gives variable results) affords 1-keto-2:3-cyclopentano-1:2:3:4-tetrahydrophenanthrene, m.p. 163—164°. Clemmensen reduction converts this ketone into 2:3-cyclopentano-1:2:3:4-tetrahydrophenanthrene, m.p. 119—121°, which with Se at 320—340° gives 2:3-cyclopentenophenanthrene, m.p. 85—85.5°.

R. S. C.

Synthesis of methylcholanthrene. E. BERGMANN and O. BLUM-BERGMANN (J. Amer. Chem. Soc., 1937, 59, 1573—1575).—5-Keto-6-methyl-5:6:7:8-tetrahydro-1:2-benzanthracene (Cook and Haslewood, A., 1934, 657) with CH₂Br-CO₂Me and Zn gives 6-methyl-5:6:7:8-tetrahydro-1:2-benzanthrylidene-5-acetic acid, m.p. 231—233° (decomp.), and its Me ester, b.p. 240—245°/1.5—2 mm., which with H₂-Pd-BaSO₄ in hot AcOH gives, after hydrolysis, 6-methyl-5:6:7:8-tetrahydro-1:2-benzanthryl-5-acetic acid, m.p. 192—194.5° (also obtained from the unsaturated acid by H₂-Pd-black in EtOAc). Ring-closure by P₂O₅ in hot C₆H₆ gives the ketone (I), m.p. 168—170°, reduced (Clemmensen) to tetrahydromethylcholanthrene, m.p. 97—99°, which with Se at 330° affords methylcholanthrene.

R. S. C.



Transformation reactions of brominated derivatives of cholesterol. IV. Experiments with dibromocholestanone. H. H. INHOFFEN (Ber., 1937, 70, [B], 1695—1701).—Treatment of dibromocholestanone with KOBz in PhMe-BuOH at 135° gives mainly the isomeric, singly unsaturated monobenzoates,

$C_{27}H_{43}O \cdot COBz$, (I), m.p. 177°, $[\alpha]_D^{20} +25.9^\circ$ in $CHCl_3$, and (II), m.p. 137—138°, $[\alpha]_D^{20} +58.0^\circ$ in $CHCl_3$. Alkaline hydrolysis of (I) leads smoothly to cholestane-3:4-dione (III), m.p. 147—148° (Butenandt *et al.*, this vol., 63), whereas under similar conditions (II) affords (III) and *cholestane-2:3-dione* (IV), m.p. (usually) 161—162° or 162—163°, $[\alpha]_D +56.9^\circ$ in $CHCl_3$ (quinoxaline derivative, $C_{33}H_{48}N_2$, m.p. 180°; *enol acetate*, m.p. 142°; *enol benzoate*, m.p. 124—124.5°). The constitution of (IV) is established by its oxidation to the dicarboxylic acid $C_{27}H_{46}O_4$, m.p. 196° (Me_2 ester, m.p. 61—61.5°), obtained by Windaus (A., 1914, i, 1066) from cholestanol. H. W.

epi-*Etiocholan-3:17-diol* from male urine. A. BUTENANDT, K. TSCHERNING, and H. DANNENBERG (Z. physiol. Chem., 1937, 248, 205—212).—Testosterone is hydrogenated ($Pd-CaCO_3$ in MeOH) to androstan-17-ol-3-one, m.p. 177—178°, and *etiocholan-17-ol-3-one* (I), m.p. 139—140°, $[\alpha]_D^{20} +32.7^\circ$ in EtOH (*acetate*, m.p. 143—144°, $[\alpha]_D^{20} +27.1^\circ$ in EtOH; *oxime*, m.p. 211—212°). (I) is reduced by Na and boiling Pr^2OH to *epi-etiocholan-3:17-diol* (II), m.p. 232°, $[\alpha]_D^{20} +26.5^\circ$ in EtOH (*diacetate*, m.p. 121—122°), identical with the product obtained from male urine (which may not exist as such in the urine but be formed during subsequent treatment). Oxidation of (II) affords *etiocholan-3:17-dione*, m.p. 128°, $[\alpha]_D^{20} +115.2^\circ$ in abs. EtOH. H. W.

Sterols. XIV. Pyroandrosterone and derivatives. R. E. MARKER, O. KAMM, D. M. JONES, and L. W. MIXON. **XV. Synthetic preparation of *epiallo-pregnanolone*, the androgenic principle of human pregnancy urine.** R. E. MARKER, O. KAMM, D. A. MCGINTY, D. M. JONES, E. L. WITTLE, T. S. OAKWOOD, and H. M. CROOKS. **XVII. Isolation of pregnanolone from human pregnancy urine.** R. E. MARKER and O. KAMM (J. Amer. Chem. Soc., 1937, 59, 1363—1366, 1367—1368, 1373—1374; cf. this vol., 416).—XIV. Oxidation of necholestene (O_3) or of β -cholestanol (CrO_3) yields a *dicarboxylic acid*, $C_{27}H_{46}O_4$, m.p. 193°, which when heated with Ac_2O to 250° gives *pyro- β -cholestanone*, m.p. 98° (pptd. by digitonin), reduced by $Al(OPr^2)_3$ to *pyro- β* (separated as digitonide), m.p. 130° (*acetate*, m.p. 77°), and *pyro-epi-cholestanol*, m.p. 155° (*acetate*, m.p. 96°), in the ratio 1:2; Na + EtOH gives a ratio 3:1. The mixed acetates of these are oxidised (CrO_3) to *pyro-* and *pyro-iso-* (pptd. as digitonide) *-androsterone*, $C_{18}H_{28}O_2$, the former, m.p. 124° (*acetate*, m.p. 102°; *semicarbazone*, m.p. 250°). Quinoline converts 3-chloroandrostan-17-one into Δ^2 -*androsten-17-one*, m.p. 102°, reduced (Na- $PrOH$) to the *androstenol*, m.p. 165°, the *acetate*, m.p. 96°, of which on ozonisation yields a *dicarboxylic acid*, $C_{19}H_{30}O_5$, m.p. 273°. Heating with Ac_2O to 250° converts this into *pyroandrostan-2-on-17-ol*, m.p. 197° (*semicarbazone*, m.p. 238°). It is concluded that the double linking in necholestene and in androstenone is in the 2:3-position.

XV. See this vol., 251.

XVII. *epi-Pregnan-20-one-3-ol*, m.p. 136° (*acetate*, m.p. 99°), the *semicarbazone*, m.p. 248°, of which is isolated from the mother-liquors after the extraction of the *epi-allo*-compound, is oxidised (CrO_3) to preg-

nanedione, m.p. 120°, and reduced (PtO_2) to a *pregnane-3:20-diol*, m.p. 230°, not pptd. by digitonin. A. LI.

Manufacture of ketones of polycyclic hydro-aromatic compounds [progesterone etc.].—See B., 1937, 842.

Manufacture of unsaturated ketones containing a sterol nucleus.—See B., 1937, 842.

Action of organo-magnesium compounds on benzilanils. (MLLES.) M. MONTAGNE and M. GARRY (Compt. rend., 1937, 204, 1659—1661).—Benzilmonoanil (I) with $MgMeI$ affords *methylbenzoinanil*, m.p. 104.5°, easily hydrolysed to methylbenzoin and NH_2Ph . $MgEtBr$, $MgEtI$, and $MgPhBr$ with (I) lead to decomp. Benzildianil with $MgMeI$ and $MgEtI$ affords, respectively, the *anils*, m.p. 154° (II) and 181° (III), of *Ph methyl-* and *ethyl-anilinobenzyl ketone* (cf. A., 1905, i, 519). The latter reaction is accompanied by the formation of (I) and $NHPhBz$. (II) with boiling HCl gives NH_2Ph and a *hydrochloride*, m.p. 145°, easily converted into 2:3-diphenyl-1-methylindole (cf. A., 1893, i, 519), whereas (III) affords NH_2Ph and an unidentified oil. J. L. D.

Synthesis of mesobenzanthrones and anthranthones by the Ullmann method. H. G. RULE and F. R. SMITH (J.C.S., 1937, 1096—1103).—8:1- $C_{10}H_6Br \cdot CO_2Me$ (A., 1934, 406) and $\sigma\text{-}C_6H_4I \cdot CO_2Me$ with Cu-bronze at 180° give crude *Me 8-o-carbonethoxyphenyl-1-naphthoate*, which in H_2SO_4 at 50° gives 75% of *mesobenzanthrone-8-carboxylic acid* and its *Me ester*, and 11% of *anthanthrone*. Substituted compounds are obtained similarly; the relative yields of benzanthrones and of anthanthrones are tabulated, and the effect of conditions and of reactivities is discussed. Benzanthronecarboxylic acids are decarboxylated by Cu-bronze in quinoline at 240°, and converted quantitatively into 8:3'-ketomesobenzanthrones by P_2O_5 in $\sigma\text{-}C_6H_4(CO)_2O$. 1'-*Bromomesobenzanthrone-8-carboxylic acid* (I), m.p. 315—316° (*Me ester*, m.p. 194°), is decarboxylated to 1'-bromomesobenzanthrone (II), identical with the product (III) from *mesobenzanthrone* (IV) and Br; the 1'-structure of (III) is thus confirmed. The product of further bromination of (IV) (G.P. 193,959) must be 6:1'-*dibromomesobenzanthrone*, since the product from (II) and Br is identical with that from decarboxylation of 6:1'-*dibromomesobenzanthrone-8-carboxylic acid*, m.p. 354—356° (decomp.). Nitration of (IV) in $PhNO_2$ at 40—50° gives the 1'- NO_2 -compound (V) (B., 1928, 598) [now obtained from the 8-carboxylic acid, m.p. 310° (decomp.)], but in boiling $AcOH$ the main product is the 2'- NO_2 -compound (B.P. 224,522; B., 1925, 583), of which the m.p. is depressed by 6-nitromesobenzanthrone, m.p. 291—292°, from the corresponding 8-carboxylic acid, m.p. 286—287° (decomp.). Oxidation (CrO_3) of (I) gives 1'-bromo-3'-hydroxymesobenzanthrone-8-carboxylic acid lactone, m.p. 321—323°. Reduction ($Na_2S_2O_4$) of (V) gives a blue vat dye which deposits a pink NH_2 -compound on atm. oxidation. *Me 6:1'-dibromo-7:8-benzomesobenzanthrone-4''-carboxylate* (VI), m.p. 233°, also forms an orange vat dye. It is obtained by brief H_2SO_4 treatment of Me_2 4:4'-dibromo-1:1'-dinaphthyl-8:8'-dicarboxylate, which

on prolonged treatment yields 4:9-dibromoanthranthrone (orange-red vat dye). A similar result is obtained with the unbrominated ester, indicating that the Me ester of type (VI) is stable whilst the acid gives an anthanthrone. Thus benzo-mesobenzanthronecarboxylic acid is converted by H_2SO_4 into anthanthrone very much more rapidly than the Me ester (where steric hindrance intervenes).

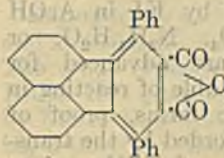
The intermediate product from Et_2 1:1'-dinaphthyl-8:8'-dicarboxylate is thus not benzomesobenzanthronecarboxylic acid (cf. A., 1914, i, 849) but the Et ester. 1:6-Dibromo- β -naphthylamine is converted (Sandmeyer) into the nitrile of 1:6-dibromo-2-naphthoic acid, m.p. 249–250°, of which the Me ester, m.p. 99–100°, yields Me_2 6:6'-dibromo-1:1'-dinaphthyl-2:2'-dicarboxylate, m.p. 220°, hydrolysed to the 2:2'-dicarboxylic acid, m.p. 342–344° (decomp.). This is converted (best by ClSO_3H) into 2:7-dibromo-anthanthrone, m.p. >360° (violet vat, dyeing cotton a deep orange). The following are also described. 5:8:1- $\text{C}_{10}\text{H}_5\text{Br}_2\text{CO}_2\text{H}$ (improved prep.); Me 5-bromo-2-iodobenzoate, m.p. 45–46°; and 2-iodo-6-nitrobenzoic acid, m.p. 188–189° [from 6-nitroanthranilic acid, new m.p. 189° (decomp.) (improved prep.)] (Me ester, m.p. 94°, from the Ag salt). Me 5-bromo-8-(o-carbomethoxyphenyl)-1-naphthoate, m.p. 155°. 1'-Bromo-8:3'-ketomesobenzanthrone, m.p. 326–328° sintering at 200°, except when resolidified and remelted, converted very slowly by alkali into a mixture (mesobenzanthrone-3'- and -8-carboxylic acids?). Me 7:8-benzomesobenzanthrone-4'-carboxylate, m.p. 154°. 6-Bromomesobenzanthrone, m.p. 182–183°, and its -8-carboxylic acid, m.p. 315–316°. 6-Bromo-, m.p. 239–240° (sintering 230°), and 6:1'-dibromo-8:3'-ketomesobenzanthrone, m.p. 299–300°. Me 5-nitro-8-o-carboxyphenyl-1-naphthoate, m.p. 154–155°. 6-Nitro-8:3'-ketomesobenzanthrone, m.p. 316–317°.

E. W. W.

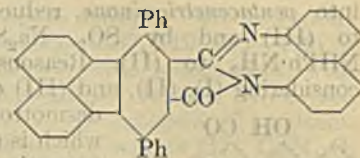
Colouring of artificial silk [with new alkoxy-mesobenzanthrones].—See B., 1937, 774.

Heteropolarity. XXIX. Adducts from maleic acid and acecylone. W. DILTHEY and S. HENKELS (J. pr. Chem., 1937, [ii], 149, 85–97).—The behaviour of the three deeply coloured ketones, tetraphenylcyclopentadienone (tetracyclone) (I), diphenyldiphenylenecyclopentadienone (phencyclone) (II), and 2:5-diphenyl-3:4-(1:8-naphthylene)- $\Delta^{2,4}$ -cyclopentadiene (acecylone) (III) (cf. A., 1935, 1241), is fundamentally similar. The endocarbonyldihydrophthalic anhydride is first formed, and loses CO when heated, giving the dihydrophthalic anhydride, which is then dehydrogenated to the highly arylated phthalic anhydride. All three products can be isolated from (I) since the temp. of the respective transformations are sufficiently removed from one another. With (II) the primary addition occurs at 80° but the temp. of evolution of CO is so close to that of dehydrogenation that the H_2 -compound can be isolated only with difficulty. With (III) the temp. of addition nearly coincides with that of decarboxylation so that the

primary product is not isolable, whereas the H_2 - and dehydro-compounds are readily obtained. (III) and maleic anhydride at >150° give 2:5-diphenyl-3:4-(1':8'-naphthylene)phthalic anhydride (acephthalide) (IV), m.p. 322°, in 95% yield, whereas in boiling PhCl the H_2 -derivative, m.p. 356°, converted when heated above its m.p. into (IV) and also produced more slowly if fumaric acid is used, is obtained. (IV) is transformed into 2:5-diphenyl-3:4-(1':8'-naphthylene)phthalic acid (V), m.p. 320°, when

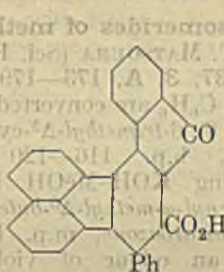


(IV.)

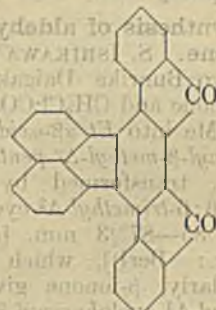


(VI.)

treated successively with NaOH-EtOH and HCl or when boiled with HCl-MeOH. The Me_2 ester of (V), m.p. 242–243°, is produced from the acid and CH_2N_2 in EtOH or from (III) and $(\text{C}\cdot\text{CO}_2\text{Me})_2$ at about 240°. Passage of NH_3 into molten (IV) affords the imide, m.p. 330–331°, whilst (IV) and molten NH_2Ph yield the anilide, m.p. 334–335°. 2:5-Diphenyl-3:4-(1':8'-naphthylene)phthaloperinone (VI), m.p. 362°, is derived from (IV) and 1:8- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ in CO_2 at 250–300°. (IV) is converted by AlCl_3 in boiling C_6H_6 into 7-phenyl-5:6-(1':8'-naphthylene)-



(VII.)



(VIII.)

fluorenone-8-carboxylic acid (VII), m.p. 341° (oxime, m.p. >400°), decarboxylated at 330–360° to 7-phenyl-5:6-(1':8'-naphthylene)fluorenone, m.p. 239–240°. (IV) is transformed by molten NaCl-AlCl_3 into 5:6-(1':8'-naphthylene)difluorenone (VIII), m.p. 351° (dioxime, m.p. >400°) reduced by Zn and AcOH in $\text{C}_6\text{H}_5\text{N}$ to 5:6-(1':8'-naphthylene)difluorenol, m.p. 245–246°, which when distilled with Zn dust gives 5:6-(1':8'-naphthylene)difluorene, m.p. 299°.

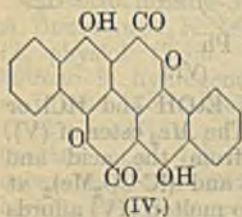
H. W.

Preparation of 4-methoxy-2:5-toluquinone. J. N. ASHLEY (J.C.S., 1937, 1471–1472).—The quinone is prepared from toluquinone and MeOH refluxed with ZnCl_2 .

R. S. C.

Linear pentacene series. C. MARSHALK (Rev. Gén. Mal. Col., 1937, 41, 353–357; cf. A., 1936, 1513).—6:13-Dihydroxy-7:12:14-triketo-5:7:12:14-tetrahydropentacene (I) (Marshalk et al., A., 1936, 1256) and the compound (II) obtained (G.P. 298,345) by condensing leucoquinizarin with o- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ in presence of AlCl_3 are oxidised to 6:13-dihydroxypentacene-5:14:7:12-diquinone (III)

(Ac_2 derivative), also obtained by acetylation of (I) followed by oxidation with PbO_2 and hydrolysis. (III) has been obtained synthetically by condensing 1:4-dihydroxyanthraquinone-2:3-dicarboxylic anhydride with C_6H_6 to 1:4-dihydroxy-2-benzoylanthraquinone-3-carboxylic acid, which is then cyclised. (III) is very readily reduced to (II), which is thus 6:7:12:13-tetrahydroxypentacene-5:14-quinone; this view is confirmed by the isolation of a tetraacetate. (II) and (III) are converted by $Pb(OAc)_2$ into pentacenetriquinone, reduced by KI in $AcOH$ to (III) and by SO_2 , $Na_2S_2O_4$, $N_2H_4 \cdot H_2O$, or $NHPh \cdot NH_2$ to (II). Reasons are advanced for considering (I), (II), and (III) capable of reacting in



desmotropic forms, proof of which is afforded by the transformation of (II) into 2:3:6:7-dibenzanthra-9:10-quinone and into 2:3:6:7-dibenz-9:10-anthrone. (II) is converted by distillation with Zn dust into 9:10-dihdropentacene in 50% yield. The product obtained by Russig by the action of air on 1:4-dihydroxy-2-naphthoic acid in alkaline solution or in org. media (considered to be a dihydroxypentacenediquinone) is (IV) since it is transformed by fusion with alkali into 1:4:1':4'-tetrahydroxy-2:2'-dinaphthyl. H. W.

Synthesis of aldehydic isomerides of methylionone. S. ISHIKAWA and T. MATSOURA (Sci. Rep. Tokyo Bunrika Daigaku, 1937, 3, A, 173—179).— α -Ionone and $CH_2Cl \cdot CO_2Et$ in C_6H_6 are converted by $NaOMe$ into *Et* α -oxido- δ -2:6:6-trimethyl- Δ^2 -cyclohexenyl- β -methyl- Δ^2 -pentenoate, b.p. 116—120°/2.5 mm., transformed by boiling KOH - $MeOH$ into γ -2:6:6-trimethyl- Δ^2 -cyclohexenyl- α -methyl- Δ^2 -butenal, b.p. 85—87°/3 mm. [*thiosemicarbazone*, m.p. 152° (corr.; Berl)], which has an odour of violets. Similarly, β -ionone gives *Et* α -oxido- δ -2:6:6-trimethyl- Δ^2 -cyclohexenyl- β -methyl- Δ^2 -pentenoate, b.p. 146—149°/2 mm., whence γ -2:6:6-trimethyl- Δ^2 -cyclohexenyl- α -methyl- Δ^2 -butenal, b.p. 131—133°/3 mm. [*thiosemicarbazone*, m.p. 160° (corr.; Berl)]. H. W.

Carbonyl constituents of eucalyptus oils. II. Seasonal variation of *E. cneorifolia* oil. P. A. BERRY, A. K. MACBETH, and T. B. SWANSON (J.C.S., 1937, 1443—1447).—The oils obtained by monthly distillations of young leaf of *E. cneorifolia* show increase during the period of active growth, and side by side with this a fall in *d*- and a rise in *l*-rotation owing to increase in the terpene content of the oil. No marked similar change is found in the oils from old leaf. The terpenes contain considerable quantities of *l*- β -phellandrene during the flush period, and the biogenetic relationship *l*- β -phellandrene, *l*-phellandral, *l*-4-isopropyl- Δ^2 -cyclohexan-1-one is suggested. *l*- α -Phellandrene and cymene are also present, the amount of the latter decreasing in the winter months. No crystal was detected. F. R. S.

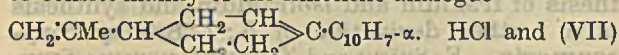
***d*-Phellandral and *d*-4-isopropyl- Δ^2 -cyclohexen-1-one.** P. A. BERRY, A. K. MACBETH, and T. B. SWANSON (J.C.S., 1937, 1448—1450).—The oil of

water-fennel contains *d*-phellandral, $\alpha_D +116.22^\circ$ (2:4-dinitrophenylhydrazone, m.p. 204°), *d*-4-isopropyl- Δ^2 -cyclohexen-1-one, $\alpha_D +52.16^\circ$ (p-nitrophenylhydrazone, m.p. 167.5°; 2:4-dinitrophenylhydrazone, m.p. 136°), and *d*- β -phellandrene, detected through the nitrosite. F. R. S.

Stability and capability of transformation of the pinane system in tertiary methylnopinol and in homologous tertiary nopinols. M. LIEP and H. STEINBRINK (J. pr. Chem., 1937, [ii], 149, 107—152).—A substituent (except $1-C_{10}H_{17}$) in addition to OH at 4 in *apopinane* diminishes the stability of the ring system during reactions, particularly during elimination of H_2O . As OH is removed with formation of a double linking, the 7:3-union is ruptured and a dicyclic system is not further formed but the bridge remains broken. Mixtures of monocyclic hydrocarbons result, a portion of which containing the double linkings in the α -terpinene position can be removed as maleic anhydride (I) adducts. The production of the same adducts from *tert*-nopinols and (I) depends on the dehydrating power of (I) which causes loss of H_2O in the initial stages of the change. The formation of hydrochlorides is explained similarly; during replacement of OH by Cl the bridge is broken with production of a double linking. This remains intact during reactions with PCl_5 but becomes saturated when HCl is used. Interaction of nopinone with the appropriate Grignard reagent gives the following compounds: methylnopinol (II), b.p. 88—89°/12 mm., m.p. 58—59°, $[\alpha]_D^{17} -2.30^\circ$ in abs. Et_2O ; ethylnopinol, m.p. 44—45°, $[\alpha]_D^{17} +3.87^\circ$ in abs. Et_2O ; n-propylnopinol, m.p. 41—42°, $[\alpha]_D^{17} +10.57^\circ$ in abs. Et_2O ; benzylpinol (III), b.p. 131—132°/0.8 mm., $[\alpha]_D^{20} +10.41^\circ$ in cyclohexane; phenylnopinol (IV), m.p. 116—117°, $[\alpha]_D^{18} +7.91^\circ$ in abs. Et_2O , and m.p. 59—60°, $[\alpha]_D^{18} +24.5^\circ$ in abs. Et_2O , respectively; 2-naphthylnopinol (VI), m.p. 120—121°, $[\alpha]_D^{20} +43.90^\circ$ in C_6H_6 ; 1-naphthylnopinol (VII), m.p. 163—164°, $[\alpha]_D^{20} +84.30^\circ$ in C_6H_6 . (II) is converted by Cl at 220° into *p*-cymene. $ZnCl_2$ dehydrates (V) in boiling C_6H_6 to a hydrocarbon, $C_{15}H_{18}$, b.p. 107—108°/0.25 mm. $H_2C_2O_4$ transforms (IV) and (V) into closely similar products, $C_{15}H_{18}$, b.p. 118—119°/1 mm. and 119—120°/1.2 mm., $[\alpha]_D^{20} -13.61^\circ$ and -40.73° in C_6H_6 , respectively, which afford the same dihydrochloride, $C_{15}H_{20}Cl_2$ (VIII), m.p. 86°, and are hydrogenated to the hydrocarbon, $C_{15}H_{22}$, b.p. 105—106°/1.4 mm. The main component is probably $\Delta^1:7^{(8)}$ -cyclohexadiene. $H_2C_2O_4$ and (II) at 130° give the strongly unsaturated substance $C_{16}H_{20}$, b.p. 125—129°/1.5 mm. With HCl in dry Et_2O (II) gives mainly dipentene dihydrochloride, (III), (IV) or (V), and (VI) similarly yield dihydrochlorides, $C_{16}H_{22}Cl_2$, m.p. 110.5—111°, $C_{15}H_{20}Cl_2$, m.p. 85—86°, and $C_{19}H_{22}Cl_2$ (IX), m.p. 107—107.5°, respectively; to these a monocyclic structure is ascribed since they are derived also from the corresponding hydrocarbons. (IV) or (V) with PCl_5 in ligroin gives a non-cryst. monohydrochloride, transformed by HCl into (VIII); under similar conditions (V) gives an unsaturated monohydrochloride, m.p. 99—100°, $[\alpha]_D^{18} -101.15^\circ$ in C_6H_6 , transformed by HCl into (IX). (II) is unaffected by borophosphoric acid in C_6H_6 . (IV) is converted by Et_3BO_3 at 100°

and then at 160° into a hydrocarbon mixture and a product $B(O\cdot C_{15}H_{19})_3$, m.p. 204—206°. Attempts to obtain the acetate of (IV) were unsuccessful. (II) and (I) at 90—100° give 3:6-endoethylene-3-methyl-6-isopropyl-1:2:3:6-tetrahydrophthalic anhydride (X), m.p. 60—61°, $[\alpha]_D^{20} \pm 0^\circ$ (corresponding imide, m.p. 156.5—157°), identical with that derived from α -terpinene. α -Phellandrene and (I) give an adduct, m.p. 127—127.5°, whereas β -phellandrene yields a complex product. Borneol and (I) at 160° afford fumaric acid and *bornyl H maleate*, m.p. 118—118.5°. *iso*Borneol and camphene hydrate appear to give mainly the corresponding normal esters. (III), (IV) or (V), and (VI) with (I) give products, $C_{20}H_{22}O_3$, m.p. 134—135°, $[\alpha]_D^{20} \pm 0^\circ$ (corresponding imide, m.p. 183—183.5°), $C_{19}H_{20}O_3$, m.p. 170.5—171°, and $C_{23}H_{22}O_3$, m.p. 201—201.5°, respectively, analogously constituted to (X). Nopinol and (I) give the adduct, $C_{13}H_{16}O_3$, m.p. 107—108°, derived from *apo*- α -terpinene.

The optically active hydrocarbon obtained from (VII) and $H_2C_2O_4$ is obviously a mixture with strongly unsaturated components; a maleic anhydride adduct cannot be obtained from it or from (VII). It appears to consist mainly of the limonene analogue



give an optically inactive *monohydrochloride* (XI), $C_{19}H_{21}Cl$, m.p. 99.5°, which is indifferent towards CaO , and is converted by $AgOAc$ into a mixture of hydrocarbons and by Mg into a somewhat unsaturated hydrocarbon, m.p. 40—42°, of ill-defined composition. Cautious treatment of it with $NaOEt$ gives the homogeneous, optically inactive *hydrocarbon*, $C_{19}H_{20}$, m.p. 55—56°, re-convertible into (XI). With Na and $EtOH$ (XI) gives an optically inactive saturated *hydrocarbon*, $C_{29}H_{24}$, b.p. 128—130°/1.5 mm., which is therefore monocyclic. (VII) and PCl_5 give the *monohydrochloride*, $C_{19}H_{21}Cl$, m.p. 90—90.5°, $[\alpha]_D^{25} -132.5^\circ$ in C_6H_6 , which appears saturated towards Br and is converted by 0.2N- $NaOEt$ into the feebly unsaturated *hydrocarbon*, $C_{19}H_{20}$, m.p. 50.5—51°, $[\alpha]_D^{25} -88.9^\circ$ in C_6H_6 . H. W.

Resolution of *cis*- and *trans*-norcaryophyllenic acid. H. N. RYDON (J.C.S., 1937, 1340—1342).—*Et cyanonorcaryophyllenate*, b.p. 133—136°/1.5 mm., obtained from *Et* $\alpha\alpha'$ -dibromo- $\beta\beta$ -dimethyladipate and $NaCN$, is hydrolysed (KOH) to 3:3-dimethylcyclobutane-1:2:2(1:1:2)-tricarboxylic acid, m.p. 176° (decomp.), decarboxylated to a mixture of *cis*- and *trans*-norcaryophyllenic acid. Resolution of the *dl-cis*-acid through the cinchonidine salt [salt of *d*-acid, m.p. 215° (decomp.), $[\alpha]_D^{20} -138.0^\circ$ in $EtOH$] gives *d*-, m.p. 163—165°, $[\alpha]_D^{20} +4.9^\circ$ in $CHCl_3$, and *l-cis*-norcaryophyllenic acid, m.p. 165°, $[\alpha]_D^{20} -5.9^\circ$ in $CHCl_3$. The *dl-trans*-acid is resolved through the brucine salt (salt of *l*-acid, $[\alpha]_D^{20} -81.46^\circ$ in $COMe_2$) into *l*-, m.p. 126°, $[\alpha]_D^{18} -129.0^\circ$ in $CHCl_3$, and *d-trans*-norcaryophyllenic acid, m.p. 123—125°, $[\alpha]_D^{18} +122.3^\circ$ in $CHCl_3$, which is identical with the *d*-acid obtained by oxidising caryophyllene. The bearing of this identity on the stereochemistry of caryophyllene is discussed, and it is pointed out that the assumption that natural products possess the most stable configuration is unjustifiable. F. R. S.

Elemic acid from manila elemi resin. IX. Dihydroelemolic acid. M. MLADENOVIC (Monatsh., 1937, 30, 405—408; cf. A., 1936, 340).—Hydrogenation ($Pd-C$ or PtO_2 ; $EtOAc$; room temp. or 60°) of elemic acid (I), purified by way of derivatives, gives only dihydroelemolic acid, m.p. 238°. When purified only by crystallisation, (I), m.p. 220°, gives also a small amount of tetrahydroelemonic acid. Ruzicka's results (A., 1933, 69) were due to the use of impure (I). R. S. C.

Sapogenins of *Polygala senega*. W. A. JACOBS and O. ISLER (J. Biol. Chem., 1937, 119, 155—170).—The crude saponin, senegin, from *senega* root, with $EtOH-HCl$ gives a *prosapogenin*, further hydrolysed by $EtOH-H_2O-HCl$ to a mixed sapogenin (I) containing a dihydroxydicarboxylic acid, *senegenin* (II), $C_{30}H_{44}O_8$ or $C_{30}H_{46}O_8$, m.p. 290—292°, $[\alpha]_D^{25} +19^\circ$ in $EtOH$ (*Me* ester). In alkali (II) opens a lactone ring and becomes tribasic, but is not regenerated on acidification. It is converted by $AcOH-NaOAc$ into the Ac_2 derivative, m.p. 270° (decomp.), and a substance, m.p. 313°. The mixture (I), after removal of (II), gives a second product, which when heated with aq. $NaOH$ yields a dihydroxydicarboxylic acid *Et* ester (III), $C_{31}H_{50}O_8$ or $C_{31}H_{48}O_8$, m.p. 257° (rapid heating) (*Na* salt; *di-p*-bromobenzoyl derivative, m.p. 213°), in which no lactone group can be detected, but which gives the *Et* ester diacetate, with a less sol. *by-product*, no m.p. <340°. With CH_3N_2 , (III) gives the *Me* *Et* ester; with $KOH-C_5H_{11}\cdot OH$, the dihydroxydicarboxylic acid, m.p. 230°, is obtained. Dehydrogenation (Se) of (II) gives products including a chrysene homologue, $C_{23}H_{22}$, m.p. 246.5°, apparently identical with Ruzicka's product from hederagenin (A., 1932, 517), with a substance, m.p. 198°, apparently trimethylpicene. Dehydrogenation of (III) gives similar products. E. W. W.

Sapogenin of *Gypsophila*. M. S. TAGGART and G. H. RICHTER (Biochem. Z., 1937, 291, 349—353; cf. Karrer and Lier, A., 1926, 401).—The sapogenin, (I), probably $OH\cdot C_{24}H_{38}\cdot CO\cdot CO_2H$ (OH alcoholic) (*hydrazone*), is a pentacyclic α -keto-acid containing no aromatic ring. The semicarbazone of (I) with Na in $EtOH$ at 180° for 8 hr. gives an acid, m.p. 302°, containing no active H. (I) treated successively at 150—160° for 10 hr. with HI and for 10 hr. with $HI + red P$ yields the corresponding hydrocarbon, $C_{26}H_{44}$, $d_4^{25} 0.9354$, $n_D^{25} 1.5029$. W. McC.

Dracorubin. II. H. BROCKMANN and R. HAASE (Ber., 1937, 70, [B], 1733—1738; cf. A., 1936, 1260).—Fresh analyses and determinations of mol. wt. of dracorubin (I), m.p. 314—315° when placed in bath preheated to 304°, $[\alpha]_D^{25} -35^\circ$ in $CHCl_3$, its hydrochloride, perchlorate, and picrate establish the composition $C_{32}H_{24}O_5$ (instead of $C_{19}H_{14}O_3$) for (I) and its "obvious identity" with the dracocarmin of Hesse (A., 1936, 1435). Treatment of (I) with molten KOH affords $COPhMe$ and $BzOH$; the latter is also obtained by the oxidation of (I) with CrO_3 or H_2O_2 . (I) is rapidly decolorised by Zn dust in $AcOH-C_5H_5N$ but not in $AcOH$ alone; the colour is restored by air. (I) is converted by Br in $CHCl_3$ into *dibromodracorubin*, decomp. about 300° (*hydrobromide*). Hydrogenation (Pt in $AcOH$) of (I) give the sparingly sol. α -hydro-

dracorubin (II), $C_{32}H_{38}O_5$ (possibly $C_{32}H_{40}O_5$), m.p. 248° (decomp.), $[\alpha]_D^{20} +74^\circ$ in C_5H_5N , which appears to contain at least one OH. Since (I) does not contain active H this OH must be formed by reduction of CO, hence fixing the function of a second O in (I). With NH_2OH (I) yields a cryst. product. $COPhMe$ is not formed by the action of molten KOH on (II); (II) is readily oxidised by air and is converted by chloranil in C_6H_6 into β -dracorubin, $C_{32}H_{30}O_5$ (? $C_{32}H_{28}O_5$), m.p. 280° (corr.), which resembles (I) very closely and may be present in the crude drug. The mechanism of dehydrogenation is not elucidated but the process occurs in two stages. Oxidation of (I) with H_2O_2 gives a yellow, cryst., optically active substance, probably $C_{24}H_{20}O_6$, m.p. 248° , which can be hydrogenated and acetylated and is capable of thermal degradation. H. W.

Butyryl derivative of Congo copal. E. MERTENS, L. HELLINCKX, and C. DE HOFFMANN (Bull. Soc. chim. Belg., 1937, 46, 253—255).—The copal is refluxed with technical abs. $PrCO_2H$ for 4 hr., and the excess of acid then distilled off at 150° . The product, m.p. 117 — 118° , consists of butyric esters of the OH-acid together with the other constituents of the copal. The *d*, acid, sap., ester., and I vals. are recorded.

H. G. M.

Preparation of tetrahydrofuran. I. T. STRUKOV (Chim. Farm. Prom., 1935, No. 1, 35).—Tetramethylene glycol is treated with $SOCl_2$ and the product treated with NaOH and redistilled. CH. ABS. (r)

Preparation of ditetrahydrofurfurylamines.—See B., 1937, 880.

Catalyst for oxidation of furfuraldehyde. V. J. SERDIUKOV (Maslob. Shir. Delo, 1934, No. 4, 43).— V_2O_5 may be replaced by V-Fe or V-Al alloys (8%V); these alloys are useful for other oxidations.

CH. ABS. (r)

Pharmaceutical application of furfuraldehyde. II. A. MANGINI (Riv. Biol., 1937, 22, 482—488).—Furfuraldehyde with *p*- or *o*-anisidine or *p*-phenetidine in $EtOH$ - $AcCO_2H$ affords 6-methoxy-, m.p. 242 — 243° (decomp.) (*Na* salt), 8-methoxy-, m.p. 230 — 231° (decomp.) (*Na* salt), and 6-ethoxy-2-(2'-furyl)cinchonic acid, m.p. 218 — 219° (decomp.) (*Na* salt), respectively. The pharmacological properties of the above acids are compared with those of other atophan derivatives.

F. O. H.

Condensation of methyl pyruvate with methyl malonate in presence of anhydrous zinc chloride. J. W. BAKER and (Miss) A. S. LAUFER (J.C.S., 1937, 1342—1348).— $AcCO_2Me$ and $CH_2(CO_2Me)_2$ (2:1 mol.) condense ($ZnCl_2$) to give *Me 2-keto-3-methyl-2:5-dihydrofuran-5-malonate-5-carboxylate* (I), m.p. 119° , and an unsaturated ester, $C_{14}H_{20}O_8$, b.p. $101^\circ/0.6$ mm. Hydrolysis of (I) with KOH yields the *Me H_2* ester, m.p. 145° (decomp.), decarboxylated to 5-carbomethoxy-2-keto-3-methyl-2:5-dihydrofuran-5-acetic acid, m.p. 144° , with $Ba(OH)_2$ affords the *Ba* salt (+4 H_2O), hydrolysed to 2-keto-3-methyl-2:5-dihydrofuran-5-malonic acid, m.p. 136° (decomp.), and with HCl forms the 5-acetic acid (II), m.p. 124° (*Me* ester, b.p. $126^\circ/1$ mm.), and α -methyl-lævulic acid (*p*-nitrophenylhydrazone, m.p. 170° ; *p*-nitrophenylhydrazone of *Me* ester, m.p. 142°). α -Methyl-lævulic

acid is obtained by hydrolysis of *Me 8-keto-n-pentane-3 γ -dicarboxylate*, b.p. $128.5^\circ/12$ mm., from $CH_3Ac\cdot COMe$ and $CHMeBr\cdot CO_2Me$, whilst the β -acid is similarly prepared through *Me 7-keto-3-methyl-n-butane- $\alpha\beta$ -dicarboxylate*, b.p. 125 — $126^\circ/11$ mm. (semicarbazone, m.p. 151°). Hydrolysis of (II) with $Ba(OH)_2$ gives α -methylmuconic acid, m.p. 171° [synthesised in a form of high m.p., 276° (decomp.), from α -methyladipic acid], and catalytic reduction yields the H_2 -acid, m.p. 96° . Reduction of (I) affords *Me 3-hydroxy-8-carbethoxy-n-pentane- $\alpha\beta$ -tricarboxylate*, m.p. 107.5° , hydrolysed to 2-keto-3-methyltetrahydrofuran-5-acetic-5-carboxylic acid, m.p. 186° . Ozonolysis of (I) gives CH_2O and $H_2C_2O_4$ and of (II) yields CH_2O , HCO_2H , and some *dl*-malic acid. The interrelationships of the derivatives are summarised.

F. R. S.

Synthesis of 6-methylcoumarin. A. M. BULUGINA (Maslob. Shir. Delo, 1934, No. 4, 43—44).—On a semi-technical scale *p*-cresol and fumaric acid with 72% H_2SO_4 give a 40% yield of 6-methylcoumarin, m.p. 73 — 74° .

CH. ABS. (r)

Natural coumarins. XXXII. Partial synthesis of fraxidin and isofraxidin and synthesis of a further derivative of 6:7:8-trihydroxycoumarin. E. SPATH and Z. JERZMANOWSKA-SIENKIEWICZOWA (Ber., 1937, 70, [B], 1672—1677).—Partial methylation of fraxetin (7:8-dihydroxy-6-methoxycoumarin) (I) with CH_3N_2 gives 8-hydroxy-6:7-dimethoxycoumarin and 7-hydroxy-6:8-dimethoxycoumarin, identical with fraxidin and isofraxidin respectively. In an attempted synthesis of (I), 6:7:8-trihydroxycoumarin [prep. from 1:2:3:4- $C_6H_2(OH)_4$ described] is partly methylated but the product (II), m.p. 223 — 224° (vac.), is not identical with (I) and is either 6:8-dihydroxy-7-methoxy- or 6:7-dihydroxy-8-methoxy-coumarin. Further, pyrogallol carbonate is converted by conc. H_2SO_4 and HNO_3 at -10° into 4-nitropyrogallol carbonate, m.p. 151 — 153° (vac.), which with CH_3N_2 in Et_2O affords 4-nitropyrogallol carbonate 3-*Me* ether, b.p. 120 — 130° (bath)/0.005 mm., m.p. 125 — 127° (vac.); this is reduced ($ZnCl_2$ -conc. HCl) to 3-amino-pyrogallol carbonate 3-*Me* ether, the hydrochloride of which is transformed by H_2O at 140 — 150° into 1:3:4-trihydroxy-2-methoxybenzene, m.p. 101 — 102.5° , and thence by malic acid and conc. H_2SO_4 at 110 — 115° into (II).

H. W.

Natural coumarins. XXXIII. Constitution of ammosesinol. E. SPATH and F. KESZTLER (Ber., 1937, 70, [B], 1679—1680).—A reply to Raudnitz (this vol., 383).

H. W.

Utilisation of phenanthrene for synthesis of dyes of the type of fluorescein and rhodamine.

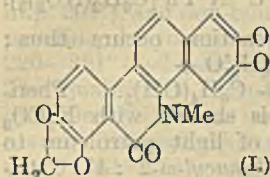
B. BOGOSLOVSKI (Prom. Org. Chim., 1937, 3, 299—300).—Diphenic anhydride (I) and *m*- $C_6H_4(OH)_2$ (II), heated with $ZnCl_2$ (210° ; 2 hr.), yield an analogue of fluorescein ($R=OH$, $R'=H$). Dyes of the type of gallein ($R=R'=OH$) or rhodamine ($R=NEt_2$, $R'=H$) are obtained by substituting gallic acid or



$m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2$ for (II) in the above reaction. The dyes are of no practical importance, both because of their poor dyeing qualities, and because of the low yields of (I) obtained by oxidation of phenanthrene.

R. T.

New nitrogenous component of *Sanguinaria canadensis*. L. E. SPATH, F. SCHLEMMER, G. SCHENCK, and A. GEMPP



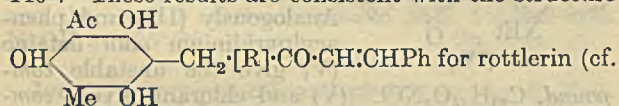
(I)

(Ber., 1937, 70, [B], 1677—1679).—Chromatographic analysis of the alkaloids in CHCl_3 by Al_2O_3 leads to the isolation of *hydroxy-sanguinarine* (I), m.p.

360—361° (vac.; corr.), $[\alpha]_D^{20} \pm 0^\circ$, also obtained by oxidation of sanguinarine nitrate by $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution.

H. W.

Rottlerin. H. BROCKMANN and K. MAIER (Naturwiss., 1937, 25, 460).—Determination as the *p*-nitrophenylhydrazone shows that 1 mol. of PhCHO is formed from 1 mol. of rottlerin (I) when the latter is ozonised. Oxidation of (I) under various conditions yields neither *o*- nor *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. The action of diazoaminobenzene on (I) yields a cryst. red dye, m.p. 206—206.5°, identified as 3-benzeneazo-2:4:6-trihydroxy-5-acetyltohuene. When (I) is boiled with EtOH , PhMe , or AcOH , it yields a yellow cryst. product, $\text{C}_{23}\text{H}_{22}\text{O}_6$ or $\text{C}_{27}\text{H}_{26}\text{O}_7$, m.p. 139—140°. These results are consistent with the structure



McGookin *et al.*, this vol., 300).

W. O. K.

Difurylmethane derivatives. D. DINELLI [with G. B. MARINI] (Gazzetta, 1937, 67, 312—317).— Et furan-2-carboxylate (I) with $(\text{CH}_2\text{O})_3$ in H_2SO_4 yields the Et_2 ester, b.p. 204°/4 mm., of 2:2'-difurylmethane-5:5'-dicarboxylic acid, m.p. 238° (also obtained by way of the Me and Me₂ esters). When distilled with Cu, this gives 2:2'-difurylmethane, and its 5-carboxylic acid, m.p. 118°. With $(\text{MeCHO})_3$ in H_2SO_4 , (I) gives the Et_2 ester, b.p. 210°/5 mm., of α -2:2'-difurylmethane-5:5'-dicarboxylic acid, m.p. 216°, decarboxylated (Cu) to the 5-carboxylic acid, m.p. 105°, and to α -2:2'-difurylmethane, b.p. 80°/10 mm. With PhCHO , (I) yields Et_2 2:2'-difurylmethane-5:5'-dicarboxylate, m.p. 212°.

E. W. W.

Amino-acids containing sulphur. I. Synthesis of 2-thienylalanine. H. C. YUAN and H. C. LI (J. Chinese Chem. Soc., 1937, 5, 214—218).—Thiophen-2-aldehyde Et_2 acetal, b.p. 223° [prep. from Mg 2-thienyl iodide and $\text{CH}(\text{OEt})_3$ described], is converted by hippuric acid, fused NaOAc , and Ac_2O at 100° into 2-phenyl-4-2'-thienylideneoxazolone, m.p. 173—174°, which is transformed by boiling aq. Na_2CO_3 into α -benzamido- β -2-thienylacrylic acid, m.p. 227—228° (decomp.). This is reduced by Na-Hg to α -benzamido- β -2-thienylpropionic acid, m.p. 177—178.5°, hydrolysed by 6N-HCl to 2-thienylalanine, m.p. 246—246.5° (decomp.) (picrolonate, decomp. above 200°).

H. W.

Manufacture of indigoid vat dyes [oxythionaphthens].—See B., 1937, 888.

Carbon compounds of the 1:9-anthrathiophen series.—See B., 1937, 880.

Structure of the sulphur black dye nigro-sulphine K. V. UFMITZEV (Prom. Org. Chim., 1937, 3, 354—359).—The results and conclusions of Chmelnitzkaja *et al.* (A., 1935, 1384) are questioned. Hydrolysis data suggest the presence of $\text{S}\cdot\text{SO}_3\text{H}$, but not of SO_3H or $\text{S}\cdot\text{SO}_2\text{H}$ groups.

R. T.

[Derivatives of cyclotetramethylenepyrrole and their molecular compounds with substituted barbituric acids.] H. RUHKOFF (Ber., 1937, 70, [B], 1835; cf. this vol., 307).—An acknowledgment of the publication of Lee and Christiansen (A., 1936, 1268).

H. W.

Pyridine-2-acetic acid. M. P. OPARINA (Chim. Farm. Prom., 1936, No. 2, 98—101).—Pyridine-2-acetic acid loses CO_2 in H_2O at 50—60°. The Me ester is more stable and may be hydrogenated (Pt) to piperidine-2-acetic acid; it yields CH_4 with Grignard reagents.

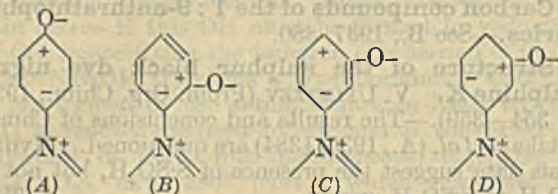
CH. ABS. (r)

2:3:6-Triaminopyridine. A. TSCHITSCHIBABIN and C. HOFFMANN (Compt. rend., 1937, 205, 153—154; cf. A., 1916, i, 163).—2:6-Diamino-3-benzene-azopyridine with $\text{H}_2\text{-Ni}$ in Ac_2O affords 2:3:6-triacetamidopyridine, m.p. 253°, hydrolysed (HCl in sealed tube) to the base (unstable in air), which is isolated as its dihydrochloride, m.p. 230° (decomp.) (block).

J. L. D.

Mesomerism of 1-hydroxyphenylpyridinium bases. W. SCHNEIDER, W. DÖBLING, and R. CORDUA (Ber., 1937, 70, [B], 1645—1665; cf. A., 1924, i, 1107).—The differing colours of solutions of phenol betaines of the type of the 1-hydroxyphenylpyridinium bases are not related to a change of mol. wt. in solution. The simple mol. wt. of the substances in EtOH is not in harmony with the existence of a bimol. red base. Substituents *ortho* to the phenolic OH influence the character and colour of the bases according to the auxochromic or antiauxochromic nature. The lightly coloured NO_2 -bases are well marked betaines since the NO_2 groups increase the anionic character of the mol. and so increase the polar contrast to the cationic character dependent on the pyridinium complex. These substituents therefore displace the condition of the mol. towards the betaine structure and also stabilise it so that solvatochromism almost disappears. NH_2 and NHAc groups act in the opposite direction, diminishing the polar contrast within the mol. The condition of the mol. is therefore displaced from the true betaine form. Solvation displaces this condition stepwise in accordance with the nature of the solvent more or less in the sense of an approximation to the betaine structure since the dipoles of the solvent are attracted to the polar centres of the mol. and stabilise the zwitterions as such and saturate the system from without. In the blue and green solutions and particularly in the solid anhydrides the mol. is farthest removed from the betaine condition; therefore the colour is deepest here and the chemical character is most unsaturated. This second, unsaturated limiting

condition, initially interpreted by a quinonoid constitution, is best expressed by the "polar quinonoid"

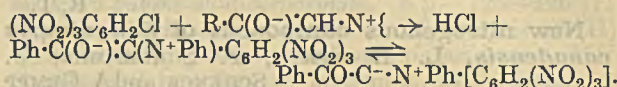


structures *A* and *B*, whilst for *m*-derivatives, which show analogous behaviour, the "polar *m*-quinonoid" constitutions *C* and *D* are available.

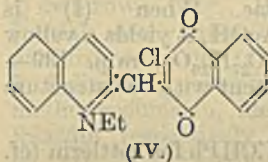
2:4:6-Triphenylpyrylium iodide, anhyd. NaOAc, and *p*-NH₂·C₆H₄·OH in boiling AcOH yield 2:4:6-triphenyl-1-*p*-hydroxyphenylpyridinium betaine, red hexahydrate (I), m.p. 199°, and blue-black anhydride (II). (I) becomes orange-yellow when cooled in liquid air whereas (II) remains unchanged. The colours of the solutions of (II) in various media are recorded, together with their changes with alterations of temp. (II) and MeI afford 2:4:6-triphenyl-1-*p*-anisylpyridinium iodide, m.p. 305—306°. 2:4:6-Triphenyl-1-*o*-hydroxyphenylpyridinium iodide (+1AcOH), m.p. 188°, gives the corresponding betaine. 2:4:6-Triphenyl-1-*m*-hydroxyphenylpyridinium iodide, m.p. 299—300°, is converted by alkali into compounds (C₂₉H₂₁ON)₃·HI and (C₂₉H₂₁ON)₁₄·HI, m.p. 135° and 153° respectively; the corresponding betaine base is non-cryst. (I) in AcOH is converted by conc. HNO₃ at room temp. into 2:4:6-triphenyl-1'-nitro-4'-hydroxyphenylpyridinium nitrate, decomp. about 175° after softening at about 145°, transformed by alkali into 2:4:6-triphenyl-1-nitro-4'-hydroxyphenylpyridinium betaine, m.p. 290°. 2:4:6-Triphenyl-1-nitro-3'-hydroxyphenylpyridinium betaine (+0.5H₂O), m.p. 345° [corresponding nitrate (+1H₂O), decomp. about 150° after softening at 130°], and 2:4:6-triphenyl-1-dinitro-2'-hydroxyphenylpyridinium betaine, m.p. about 335° on block preheated to 330° (corresponding nitrate, m.p. about 340°), are described. Reduction of the NO₂-compounds gives the corresponding amines. The readily oxidised 2:4:6-triphenyl-1-amino-4'-hydroxyphenylpyridinium betaine is isolated as the benzoate, C₂₉H₂₂ON₂·2BzOH, m.p. 219—220°, transformed by hot Ac₂O into 2:4:6-triphenyl-1-acetamido-4'-hydroxyphenylpyridinium betaine (+6H₂O), m.p. 198—200°. 2:4:6-Triphenyl-1-amino-3'-hydroxyphenylpyridinium betaine gives a chloride (+1H₂O), m.p. 207—208°, converted by Ac₂O + NaOAc into 2:4:6-triphenyl-1'-acetamido-3'-hydroxyphenylpyridinium betaine (+4H₂O), m.p. 163—164°. 2:4:6-Triphenyl-1-diamino-2'-hydroxyphenylpyridinium betaine is transformed by NaOAc and Ac₂O into the Ac₂ derivative, the chloride of which has m.p. 225—226° after softening at 210°. 2:4:6-Triphenyl-1-*m*-methoxyphenylpyridinium iodide, m.p. 232°, is converted by conc. HNO₃ in AcOH at 100° into the substance C₃₀H₂₃O₃N₂I, m.p. (indef.) 140°, reduced to a non-cryst. amine, which gives a pure yellow solution in CHCl₃. H. W.

Enol betaines. VII. Explanation of the colour reactions with picryl chloride and chloranil. F. KRÖHNKE and H. SCHEISS (Ber., 1937, 70, [B],

1728—1732).—The formation of coloured compounds in the reaction between picryl chloride (I) and phenacylcyclammonium salts is attributed to mesomerism as shown by the scheme.

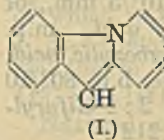


With quinones a similar reaction occurs thus: Ph·C(O):CH·N⁺C₅H₅ + 2O:C₆H₄:O → Ph·C(O):C(C₆H₃O₂)·N⁺C₅H₅ + C₆H₄(OH)₂. Phenacylpyridinium salt in H₂O is shaken with K₂CO₃ and (I) in CHCl₃; addition of light petroleum to the CHCl₃ solution ppts. phenacyl-ω-2':4':6'-trinitrophenylpyridinium enol betaine (II), m.p. 142° (decomp.) (perchlorate, m.p. about 75°). When heated with 5*N*-HCl (II) yields BzOH. Phenacyl-ω-2':4'-dinitrophenylpyridinium enol betaine, m.p. 187° (decomp.) (perchlorate, m.p. 157°), yields BzOH when warmed with *N*-NaOH at 50°. Phenacyl-ω-5'-chloro-2':4'-dinitrophenylpyridinium enol betaine has m.p. 167° (decomp.). *p*-Methylphenacyl-ω-2':4':6'-trinitrophenylpyridinium enol betaine, m.p. 168—169°, is described. Phenacyl-ω-2':4':6'-trinitrophenylisoquinolinium enol betaine, m.p. 119—120° (decomp.), gives a mono- and dihydrate. 2-Methylquinoline ethiodide and 2:3-dichloro-α-naphthaquinone (III) afford the compound (IV), which becomes grey at 170—177°. Analogously (III) and phenacylpyridinium enol betaine (V) give the unstable compound, C₂₃H₁₄O₃NCl. (V) and chloranil give a compound, m.p. 185°, whilst (V) and C₆H₃(NO₂)₃ give the adduct, m.p. 152° (decomp.). H. W.



Werner complexes. Dissimulation of the N-H vibration in ammine complexes.—See A., I, 443.

New type of indole base. J. VON BRAUN and J. NELLES [with A. MAY] (Ber., 1937, 70, [B], 1767—1776).—4-Benzylpyridine is almost unchanged when passed over reduced Cu turnings at 580—590° whereas the 2-benzyl compound is transformed into the indole base (I), m.p. 175—176° (hydrochloride, m.p. 132°; picrate, m.p. 138°; methiodide, m.p. 231°). Alkali and most acids have little action on (I) but AcOH



causes a profound change. The green NO-compound, m.p. 221—223°, gives colourless solutions in acids; it gives a methiodide, m.p. 190°. Reduction of (I) with Na and EtOH or, preferably, amyl alcohol gives the H₄-derivative, b.p. 152—154°/0.3 mm., m.p. 56° (methiodide, m.p. 127°; methochloride, m.p. 211°; platinichloride, m.p. 197°; 3:5-dinitroso-1:2-tetramethyleneindole hydrochloride). Reduction of (I) with Sn and HCl gives the H₆-compound, b.p. 118—122°/0.25 mm., m.p. 26° (hydrochloride, m.p. 150°; picrate, m.p. 132°; NO-derivative, m.p. 227°; methiodide, m.p. 140°; methochloride, m.p. 95°, and the corresponding platinichloride, m.p. 194°). 2-Methylpyridine and CH₂PhCl give a quaternary chloride, m.p. 95°, converted by heating with Cu into a mixture of

4-benzyl-2-methylpyridine, b.p. 154°/13 mm. (picrate, m.p. 117°), which is unchanged at 580°, and 6-benzyl-2-methylpyridine, b.p. 150°/14 mm. (picrate, m.p. 147°), which passes with loss of Me into the base (I). The hygroscopic quaternary chloride, m.p. 162°, from $2\text{-C}_{10}\text{H}_7\text{-CH}_2\text{Cl}$ and $\text{C}_5\text{H}_5\text{N}$ gives 4-2'-naphthylmethylpyridine, m.p. 78° (picrate, m.p. 175°; hydrochloride, m.p. 201°), and non-homogeneous 2-2'-naphthylmethylpyridine, dehydrogenated to the base, $\text{C}_{16}\text{H}_{13}\text{N}$, m.p. 220—221° (hydrochloride, m.p. 85°; picrate, m.p. 128°). The quaternary compound from CH_2PhCl and isoquinoline (II) when heated in presence of Cu yields mainly 1-benzylisoquinoline, m.p. 50—52° (picrate, m.p. 182—184°; hydrochloride, m.p. 179—181°; platinichloride, decomp. 216—218°). This is dehydrogenated to the compound (III), $\text{C}_{16}\text{H}_{11}\text{N}$, m.p. 238°, which has only feebly basic character. It is reduced by Sn and HCl to the H_4 -compound, b.p. 170—175°/0.6 mm. (hydrochloride, m.p. 155—157°; picrate, m.p. 139—140°; platinichloride, m.p. 180°; methiodide, m.p. 217°), which could not be acetylated and is oxidised by HNO_3 mainly to $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$. The quaternary compound, m.p. 210—212°, from (II) and $\text{o-C}_6\text{H}_4\text{Me-CH}_2\text{Cl}$ yields the substance, $\text{C}_{17}\text{H}_{15}\text{N}$, m.p. 60—62° (picrate, m.p. 180—181°), which is dehydrogenated to (III). H. W.

Preparation of 8-hydroxyquinoline. O. J. MAGIDSON (Chim. Farm. Prom., 1935, No. 1, 20—23).—Quinoline is sulphonated at 160° with 20% oleum and the Ca salt of the sulphonic acid treated with NaOH at 225°/17—18 atm. CH. ABS. (r)

Iodohydroxyquinolinesulphonic acid. S. VIN-AVER (Chim. Farm. Prom., 1935, No. 2, 109—110).—Hydroxyquinolinesulphonic acid is best iodinated by addition of I to the Na salt. CH. ABS. (r)

2:6- and 2:8-dimethyl-4-chloroquinolines. General properties. Reaction with amines. A. MEYER and H. DRUTEL (Compt. rend., 1937, 205, 148—151; cf. this vol., 389).—The Na derivatives of 4-hydroxy-2:6- and -2:8-dimethylquinoline with PCl_5 , POCl_3 , or SOCl_2 afford 4-chloro-2:6- (I), m.p. 63.5°, and -2:8-dimethylquinoline (II), m.p. 72°, respectively. With NH_2Ph , $p\text{-C}_6\text{H}_4\text{Me-NH}_2$, and $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$ (I) and (II) in boiling AcOH give 4-anilino-2:6-, m.p. 172°, and -2:8-, m.p. 121°, 4-p-toluidino-2:8-, m.p. 127—128°, and 4- α -naphthylamino-2:8-dimethylquinoline, m.p. 155—156°, respectively, which afford cryst. salts and quaternary NH_4 compounds. $\text{o-C}_6\text{H}_4\text{Me-NH}_2$ and $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$ do not react. $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and benzidine each react with 2 mols. of (I) and (II) to give bases isolated as their acetates, viz.: $p\text{-phenylenedi-4-(2:6-}$, m.p. 325—327° (decomp.), and $-(2:8\text{-dimethylquinolinyl)-amine} + 2\text{AcOH}$, m.p. 309—310° (decomp.); $pp\text{'-diphenyldi-4:4'-(2:6-}$, m.p. 320—322° (decomp.), and $-(2:8\text{-dimethylquinolinyl)-amine} + 2\text{AcOH}$ (III), m.p. 305—307° (decomp.). With dil. NaOH (III) gives the free base, m.p. 233—234°. With piperazine (I) and (II) give similarly NN-di-4-(2:6-, m.p. 322—324°, and $-(2:8\text{-dimethylquinolyl)-piperazine}$, m.p. 319—320°, respectively. When boiled with NH_2Me , NH_2Et , NH_2Et_2 , and NHPH_2 (I) and (II)

lose Cl to give the acetates of the corresponding OH-compounds. J. L. D.

Carboxylic acid amides derived from azacompounds.—See B., 1937, 880.

Claisen-type condensations with quinaldine and related ammono-ketone ethers. F. W. BERGSTROM and A. MOFFAT (J. Amer. Chem. Soc., 1937, 59, 1494—1497).—Quinaldine, EtOBz, and KNH_2 (2.5 mols.) in Et_2O give 2-phenacylquinoline (I), m.p. 116.4—117.1°. Similarly are prepared 2-p-bromo-, m.p. 165.7—167.2°, 2-o-chloro-, m.p. 115.9—117°, 2-p-methoxy-, m.p. 154.5—155°, and 2-p-methyl-phenacylquinoline, m.p. 170—171°, ω -furoyl-quinaldine, m.p. 102.9—103.4°, 2-phenacyl-, m.p. 207.8—208.8°, and 2-p-methoxyphenacyl-5:6-benzquinoline (II), m.p. 158—158.5°, 3-phenacyl-2-methyl-, m.p. 125.6—126.5°, and 2:3-diphenacyl-quinoxaline, m.p. 204.5—205.2°. The alternative structure, 1-benzoyl-2-methylene-1:2-dihydroquinoline etc., is not excluded, but is less probable. The substances are weak bases, giving hydrochlorides which dissociate in H_2O , and ketonic derivatives could not be obtained. Aliphatic esters do not undergo the condensation, nor can AcCl, BzCl, $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{Et}$, or $p\text{-OH-C}_6\text{H}_4\text{-CO}_2\text{Et}$ be used; 2-n-propyl-, 4-methyl-, and 2:4-dimethyl-quinoline could not be used owing to the insolubility of the K salts. Reduction of (I) could not be effected; KMnO_4 gave only BzOH; Br (4 equivs.) gives tribromoquinaldine (II), but 6 equivs. gives also BzBr. Bromination of (II) gives (III) (30), $p\text{-OMe-C}_6\text{H}_4\text{-COBr}$ (22), and $p\text{-OMe-C}_6\text{H}_4\text{-CO}_2\text{H}$ (17%). R. S. C.

Heterocyclic compounds. II. Synthesis of 5-keto-2:3:5:6-tetrahydro- α -quinindene derivatives. S. Z. AHMAD and R. S. DESAI (Proc. Indian Acad. Sci., 1937, 5, A, 543—550).—Equimol. amounts of Et cyclopentanone-2-carboxylate (I) and NH_2Ph at 155—160° afford cyclopentanone-2-carboxyanilide and the cyclised form 5-keto-2:3:5:6-tetrahydro- α -quinindene (cf. A., 1929, 1312). Similarly (I) and $p\text{-C}_6\text{H}_4\text{Me-NH}_2$ afford cyclopentanone-2-carboxy-p-toluidide, m.p. 130°, and 1-p-tolylamino- $\Delta^{1:2}$ -cyclopentene-2-carboxy-p-toluidide, m.p. 143°; the former alone is cyclised (conc. H_2SO_4 at 100°) to 5-keto-10-methyl-2:3:5:6-tetrahydro- α -quinindene, m.p. 295°. Similarly (I) and m-4-xylidine afford cyclopentanone-2-carboxyxylylidide, m.p. 107—108°, cyclised to 5-keto-9:10-(or ? 10:11-)dimethyl-2:3:5:6-tetrahydro- α -quinindene, m.p. 280°, and 1-xylidino- $\Delta^{1:2}$ -cyclopentene-2-carboxyxylylidide, m.p. 184°. Similarly (I) with the appropriate amine affords: 1-p-chloroanilino- $\Delta^{1:2}$ -cyclopentene-2-carboxy-p-chloroanilide, m.p. 173—174°, 1-p-bromoanilino- $\Delta^{1:2}$ -cyclopentene-2-carboxy-p-bromoanilide, m.p. 179°, 1-o-anisidino- $\Delta^{1:2}$ -cyclopentene-2-carboxy-o-anisidide, m.p. 130—131°, 1- α -naphthylamino- $\Delta^{1:2}$ -cyclopentene-2-carboxy- α -naphthalide, m.p. 164°, and 1- β -naphthylamino- $\Delta^{1:2}$ -cyclopentene-2-carboxy- β -naphthalide, m.p. 184°. None of these compounds is cyclised with conc. H_2SO_4 . 4-Methylcyclopentanone-2-carboxylate (II) with NH_2Ph and $p\text{-C}_6\text{H}_4\text{Me-NH}_2$ affords products which cannot be obtained cryst., but are cyclised (warm conc. H_2SO_4) to 5-keto-, m.p. 249°, and 5-keto-2:10-dimethyl-, m.p. 230—231°, -2:3:5:6-tetrahydro- α -quinindene,

respectively. Similarly treated (II) and *m*-4-xylydine afford 4-methylcyclopentanone-2-carboxy-xylydide, m.p. 114°, cyclised to 5-keto-2:9:10- (or ? 2:10:11-)trimethyl-2:3:5:6-tetrahydro- α -quinindene, m.p. 215°, and 1-xylydino-4-methyl- $\Delta^{1:2}$ -cyclopentene-2-carboxyxylydide, m.p. 180°. Similarly (II) with *p*-C₆H₄Cl·NH₂ and *p*-C₆H₄Br·NH₂ affords 1-*p*-chloroanilino-4-methyl- $\Delta^{1:2}$ -cyclopentene-2-carboxy-*p*-chloroanilide, m.p. 167–168° and 1-*p*-bromoanilino-4-methyl- $\Delta^{1:2}$ -cyclopentene-2-carboxy-*p*-bromoanilide, m.p. 185°, respectively. When (II) is boiled with an arylamine for a few min. a *s*-diaryl-carbamide is formed. J. L. D.

Friedel-Crafts reaction. I. Synthesis of new pharmaceutical compounds. P. KRANZLEIN (Ber., 1937, 70, [B], 1776–1787).—4-Amino-*o*-xylene is converted by AcCl and C₅H₅N into 4-acetamido-*o*-xylene, m.p. 96.5°, which gives 4-acetamido-5-chloroacetyl-*o*-xylene, m.p. 167°; this, in MeOH-H₂O, is treated successively with NaOH and air whereby 5:6:5':6'-tetramethylindigotin is obtained, which is oxidised by HNO₃-CrO₃ to 5:6-dimethylisatin (I), m.p. 214–215°. Attempts to obtain (I) directly from 5:6-dimethylindoxyl were unsuccessful. CPhMe, (I), and 33% KOH at 100° yield 2-phenyl-6:7-dimethylquinoline-4-carboxylic acid (dimethylatophan) (II), m.p. 251.5°. 2-Acetamido-5:6:7:8-tetrahydronaphthalene, m.p. 106°, is converted by CH₂Cl·COCl and AlCl₃ in CS₂ into 2-acetamido-3-chloroacetyl-5:6:7:8-tetrahydronaphthalene, m.p. 148°, and thence into 5:6:5':6'-dicyclopentamethyleneindigotin, which is oxidised to 5:6-cyclopentamethyleneisatin, m.p. 194°. This is converted by CPhMe and 33% KOH into 2-phenyl-6:7-cyclopentamethylenequinoline-4-carboxylic acid (III), m.p. 237°. 5-Acetamidohydrindene, m.p. 104°, affords successively 5-acetamido-6-chloroacetylhydrindene, m.p. 167°, 5:6:5':6'-dicyclopentamethyleneindigotin, 5:6-cyclopentamethyleneisatin, m.p. 206°, and 2-phenyl-6:7-cyclopentamethylenequinoline-4-carboxylic acid (IV), m.p. 261°. (II), (III), and (IV) are probably slightly more toxic than atophan; they have no vitamin-B₂ action and have no advantage over other atophan preps. with respect to uric acid metabolism.

o-C₆H₄Cl·COCl, 1:2:4-C₆H₃Me₂·NHAc, and AlCl₃ in CS₂ afford 2'-chloro-2-acetamido-4:5-dimethylbenzophenone, m.p. 173°, hydrolysed by cold, dil. NaOH to 2'-chloro-2-amino-4:5-dimethylbenzophenone, m.p. 120°. *o*-C₆H₄Cl·CO₂H, *o*-4-xylydine, K₂CO₃, and Cu powder give 3':4'-dimethyldiphenylamine-2-carboxylic acid, m.p. 188–189°, converted by conc. H₂SO₄ at 80° or, less advantageously, by P₂O₅ in PhNO₂ into 2:3-dimethylacridone, m.p. 297°. This is reduced by Na and boiling amyl alcohol to 2:3-dimethyl-5:10-dihydroacridine, m.p. 215°, oxidised by FeCl₃ to 2:3-dimethylacridine (V), m.p. 162°. 3':4'-cyclo-Tetramethylenediphenylamine-2-carboxylic acid, m.p. 173°, is cyclised by conc. H₂SO₄ at 80° to 2:3-cyclo-tetramethyleneacridone, m.p. 309°; this is reduced by Na and boiling amyl alcohol to 2:3-cyclopentamethylene-5:10-dihydroacridine, m.p. 169–170°, oxidised (FeCl₃) to 2:3-cyclopentamethyleneacridine (VI), m.p. 117°. 3':4'-cyclo-Trimethylenediphenylamine-2-carboxylic acid, m.p. 176°, yields successively 2:3-

cyclo-trimethyleneacridone, m.p. 338°, 2:3-cyclo-trimethylene-5:10-dihydroacridine, m.p. 209°, and 2:3-cyclo-trimethyleneacridine (VII), m.p. 152°. Physiologically, substitution in the 2:3-position by alkyl or cycloalkyl groups appears to diminish the toxicity of acridine and also weakens its disinfecting action. The effect is similar to that observed by Kuhn in the flavin series. H. W.

6:9-Diamino-2-ethoxyacridine. M. BAZURIN (Chim. Farm. Prom., 1935, No. 2, 108–109).—6-Nitro-9-amino-2-ethoxyacridine is best reduced with Fe filings in slightly acid or neutral solution.

CH. ABS. (r)

Synthesis of anthrapyridines [azanthracenes]. J. VON BRAUN and J. NELLES (Ber., 1937, 70, [B], 1760–1766).—The synthesis of β -azanthracenes is described: *o*-C₆H₄Me·CH₂Cl and C₅H₅N give the quaternary chloride, m.p. 183°, converted by Cu powder at 250° into dixylypyridine, b.p. 190–195°/0.4 mm., and a mixture (I) of monoxypyridines from which *picrates*, m.p. 156–158° (derived from the 2-) and m.p. 136–138° (derived from the 4-compound), respectively, are isolated. Ring-closure of (I) is caused with difficulty by pumice, pumice-PbO₂, or S and is best effected by Cu turnings at 580–590°, whereby α -azanthracene (II), m.p. 114°, and β -azanthracene (III) (hydrochloride, m.p. 235°; methiodide, m.p. 255°; *picrate*, m.p. 248–250°), are obtained. Treatment of (III) with CrO₃ in AcOH gives the corresponding quinone, m.p. 189–190°, whereas Sn and HCl transform it into the H₄-base, m.p. 147°. The quaternary chloride, m.p. 154–156°, from 2-methylpyridine and *o*-C₆H₄Me·CH₂Cl gives a mixture (from which *picrates*, m.p. 145°, and m.p. 148–149°, respectively, are prepared), which is dehydrogenated at 580° to a methyl- β -azanthracene, m.p. 175–183°. C₅H₅N and 2:4-C₆H₃Me₂·CH₂Cl rapidly afford a non-cryst. quaternary compound, converted by Cu into a mixture of bases (*picrates*, m.p. 170–174° after softening at 150°) which at 580° gives the homogeneous base, C₁₄H₁₁N, m.p. 170–180° (hydrochloride, m.p. 244–245°). The hygroscopic quaternary compound from C₆H₅N and 1:3-dimethyl-4:6-dichloromethylbenzene yields a mixture of bases from which a *product*, C₂₆H₂₀N₂, m.p. 142°, is isolated. The amount of material is inadequate for further work but the two-sided condensation with the base is established. H. W.

Manufacture of 4-hydroxynaphthostyryl and its substitution products.—See B., 1937, 880.

Preparation of anthraquinone derivatives.—See B., 1937, 880.

Barbituric acid derivatives. II. Comparison of 2-thiol compounds of 4-imino-5-methylthio-barbituric acid and 5-methylbarbituric acid. T. NISHIKAWA (J. Chem. Soc. Japan, 1935, 56, 1487–1494).—The prep. and properties of the 2-Me, -Et, -Prⁿ, -Buⁿ, and -Bu^s derivatives of 4-imino-5-methylthio- and 5-methylthio-barbituric acids are described. Theoretical explanations are advanced for the observed differences in properties. CH. ABS. (r)

Carbylamines. XXI. Reaction with 1-phenyl-3-methyl-5-pyrazolone. M. PASSERINI and V. CASINI (Gazzetta, 1937, 67, 332—336).—When boiled with PhNC in C_6H_6 , this pyrazolone yields the *anil*, m.p. 153—155°, of 1-phenyl-3-methyl-5-pyrazolone-4-aldehyde, m.p. 173—175° (phenylhydrazone, m.p. 158—159°), converted by boiling H_2O into methenylbis-(1-phenyl-3-methyl-5-pyrazolone). E. W. W.

Catalytic fission of the glyoxaline ring. S. EDLACHER and A. VON SEGESSER (Naturwiss., 1937, 25, 556—557; cf. this vol., 307).—Elimination of 2 mols. of NH_3 is accompanied by loss of 2 mols. of CO_2 during the catalytic fission of histidine by ascorbic acid (I) and traces of Fe. Identical results are obtained with *l*-, *d*-, or *dl*-histidine monohydrochloride; this may be due to the high concn. of (I). The formation of histamine could not be observed.

H. W.

[Derivatives of cyclotetramethylenepyrazole and their molecular compounds with substituted barbituric acids.] J. LEE (Ber., 1937, 70, [B], 1835).—A claim for priority against Ruhkopf (this vol., 307).

H. W.

Piperazine. S. VINAVER (Chim. Farm. Prom., 1934, No. 6, 11—14).— p - $C_6H_4Me \cdot SO_2 \cdot NH_2$ and $(CH_2Br)_2$ are condensed and the resulting ditoluene-sulphonylpiperazine is decomposed with H_2SO_4 . Medicinally the H tartrate is preferable to the free base.

CH. ABS. (r)

Hydrogen cyanide. X. The tetrapolymeride. L. E. HINKEL, G. O. RICHARDS, and O. THOMAS (J.C.S., 1937, 1432—1437).—The previous evidence for the structure of the polymerised form of HCN is critically reviewed, and in support of the quadrimol. structure the following evidence is adduced indicating it to be aminoiminosuccinonitrile (I). With $(CHO)_2$, (I), m.p. 181° (decomp.) (hydrochloride, decomp. 134°), affords a substance, $C_6H_4ON_4$, decomp. 240°, converted by boiling aq. $H_2C_2O_4$ into 6-hydroxy-2:3-dicyanodihydropyrazine, m.p. 132°, hydrolysed (Na_2O_2) to pyrazinedicarboxylic acid. With the appropriate aldehyde, (I) yields benzylidene- (II), m.p. 191° (decomp.), salicylidene-, m.p. 234° (decomp.), m-bromosalicylidene-, m.p. 250°, anisylidene-, m.p. 227° (decomp.), and isobutylidene-aminoiminosuccinonitrile, m.p. 91° (decomp.). With Ac_2O , (I) affords successively acetamidoiminosuccinonitrile (III), m.p. 164° (decomp.), and acetamidoacetimidossuccinonitrile, m.p. 224° (decomp.); (II) with Ac_2O yields benzylidene-aminoacetimidossuccinonitrile, m.p. 227° (decomp.). With Ac_2 , (I) affords 2:3-dicyano-5:6-dimethylpyrazine, m.p. 171°, hydrolysed (Na_2O_2) to 2:3-dimethylpyrazinedicarboxylic acid, and with Bz_2 , 2:3-dicyano-5:6-diphenylpyrazine, m.p. 246°. With HNO_2 (I) yields 4:5-dicyano-1:2:3-triazole, hydrolysed to 1:2:3-triazole-4:5-dicarboxylic acid, whilst (III) with HNO_2 gives 4(or 5)-cyano-1:2:3-triazole-5(or 4)-carboxylamide, m.p. 219° (decomp.). Oxidation (nitrous fumes) of (II) gives 4:5-dicyano-2-phenylglyoxaline, m.p. 261° (decomp.), hydrolysed ($NaOH$ -EtOH) to 2-phenylglyoxaline-4:5-dicarboxylic acid.

J. D. R.

[Condensation of] 2-aminopyridine [with ethyl acetoacetate]. G. B. CRIPPA and E. SCEVOLA (Gazzetta, 1937, 67, 327—332).— $2-C_5H_4N \cdot NH_2$ (I) and $CEt_2(COCl)_2$ in C_5H_5N form diethylmalonbis-(2-aminopyridine), m.p. 115°. With $CH_3Ac \cdot CO_2Et$ and conc. HCl at 150—180°, (I) gives first 2-acetoacetamidopyridine, new m.p. 84° (cf. A., 1911, i, 327), which readily loses H_2O to give 4-keto-6-methyl-1:4-dihydropyridino-1':2':1:2-pyrimidine (II), m.p. 123° (hydrochloride).

E. W. W.

Relation between taste and chemical constitution. Naphthoisotriazine group. I. A. NERI and G. GRIMALDI. II. III. A. NERI (Gazzetta, 1937, 67, 273—282, 282—288, 289—293).—I. 1-*p*-Sulphobenzeneazo- β -naphthylamine (I) (as Na salt) and PhCHO in AcOH yield 3-phenyl-2-*p*-sulphophenyl-2:3-dihydro-1:2:4-naphthoisotriazine, no m.p., sweet (Na salt). 2:6- $NH_2 \cdot C_{10}H_6 \cdot SO_3H$ and PhN_2Cl give 1-benzeneazo- β -naphthylamine-6-sulphonic acid (II) (Na salt), which with $NaOAc$ -AcOH-PhCHO yields 2:3-diphenyl-2:3-dihydro-1:2:4-naphthoisotriazine-8-sulphonic acid, bitter (Na salt, $+6H_2O$). Similarly 1-*p*-sulphobenzeneazo- β -naphthylamine-6-sulphonic acid (III) gives 3-phenyl-2-*p*-sulphophenyl-2:3-dihydro-1:2:4-naphthoisotriazine-8-sulphonic acid, very sweet. 2-Benzeneazo- α -naphthylamine-4-sulphonic acid (IV) yields 2:3-diphenyl-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonic acid, tasteless; the 2-*p*-sulphobenzeneazo-acid (V) gives the 2-phenyl-3-*p*-sulphophenyl-sulphonic acid, sweet (Na salt, $+7H_2O$). Sweetness thus apparently depends on *p*- SO_3H being attached to *N*-Ph.

II. With *o*- $OH \cdot C_6H_4 \cdot CHO$ in AcOH, (IV) yields 3-phenyl-2-*o*-hydroxyphenyl-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonic acid, tasteless (Na salt, $+2.5 H_2O$); the corresponding 3-*p*-sulphophenyl-sulphonic acid, from (II), is sweet. Similarly (I) gives 2-*p*-sulphophenyl-3-*o*-hydroxyphenyl-2:3-dihydro-1:2:4-naphthoisotriazine, tasteless (Na salt, $+2.5 H_2O$), and (II) yields 2-phenyl-3-*o*-hydroxyphenyl-2:3-dihydro-1:2:4-naphthoisotriazine-8-sulphonic acid, bitter, whilst (III) gives the corresponding 2-*p*-sulphophenyl-sulphonic acid, tasteless. In this group *p*- SO_3H attached to *N*-Ph is not sufficient to cause sweetness.

III. With 35% CH_2O in AcOH, (IV) gives 3-phenyl-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonic acid, bitter (Na salt, $+4.5H_2O$), and (V) the corresponding 3-*p*-sulphophenyl-sulphonic acid, tasteless. From (I), 2-*p*-sulphophenyl-2:3-dihydro-1:2:4-naphthoisotriazine, tasteless, is obtained, whilst from (II), 2-phenyl-2:3-dihydro-1:2:4-naphthoisotriazine-8-sulphonic acid, bitter, and from (III), the corresponding 2-*p*-sulphophenyl-sulphonic acid, of salt taste, are prepared.

E. W. W.

Manufacture of vat dyes of the anthraquinone series.—See B., 1937, 887.

Optical absorption of porphyrins. XI.—See A., I, 442.

Acetylenic thioamides. D. E. WORRALL (J. Amer. Chem. Soc., 1937, 59, 1486—1487).— $CPh \cdot CNa$

and MeNCS give γ -phenylpropiolthiomethylamide (I), m.p. 78—80° (decomp.), giving with alcoholic alkali NH_2Me and COPhMe amongst other products, but not polymerising even in alkali. CPh_2CNa and $\text{CH}_2\text{:CH:CH}_2\text{:NCS}$ give γ -phenylpropiolthioallylamide (II), m.p. 60—61°, unstable when solid or in EtOH, but stable in Et_2O , and not polymerised by NH_3 . With $\text{NH}_2\text{OH} \cdot \text{EtOH}$ (I) and (II) give 3-methyl-, m.p. 112—113° (dibromide), and 3-allyl-amino-5-phenylisooxazole, m.p. 102—103°, respectively; in conc. solutions (II) gives also 2-phenacylthiazole, m.p. 168—169° (decomp.) after sintering, which is the main product if only 1 mol. of NH_2OH is used. With N_2H_4 (I) and (II) give (?) 3-(5'-thio-3'-phenylpyrazolyl-2'-)-5-phenylpyrazole, m.p. 169—170° (converted by conc. H_2SO_4 into CO_2 and COPhMe), but (II) gives also some 3-allylamino-5-phenylpyrazole, m.p. 98°. R. S. C.

Physical constants of morpholine. V. H. DERMER and O. C. DERMER (J. Amer. Chem. Soc., 1937, 59, 1148—1149).—Physical consts. of morpholine, b.p. 128.9°, f.p. $-4.9 \pm 0.1^\circ$, purified, if necessary *via* the H oxalate, are recorded.

R. S. C.

Phenolic morpholines etc.—See B., 1937, 981.

Benzthiazyl disulphides.—See B., 1937, 880.

Intermediates for dyes [benzthi- and benz-selen-azolines].—See B., 1937, 880.

Anthraquinone derivatives (anthraselen-azoles).—See B., 1937, 881.

Iodo-derivatives of thiodiazolines of formaldehyde. H. WUYTS and W. DESHOMMES (Bull. Soc. chim. Belg., 1937, 46, 231—240).— β -Thio-*p*-toluoyl- α -phenylhydrazine with CH_2O in EtOH-HCl gives 3-phenyl-5-*p*-tolyl-2:3-dihydro-1:3:4-thiodiazole, m.p. 111—112°, which with 6 I in CHCl_3 gives a I_5 -derivative (I), m.p. 109°, with the formation of 1 mol. of HI; with excess of I a I_7 -derivative, m.p. 116°, is also obtained. When dissolved in COMe_2 and pptd. with Et_2O (I) readily loses 2 I to give a I_3 -derivative, m.p. 106°. By similar methods 3-phenyl-5- α -naphthyl-2:3-dihydro-1:3:4-thiodiazole yields a I_5 - (II), m.p. 118°, and a I_3 - (III), m.p. 145.5°, -derivative; 3:5-diphenyl-2:3-dihydro-1:3:4-thiodiazole gives I_5 -, m.p. 98°, and I_3 -, m.p. 151.5°, -derivatives; and 3-phenyl-5-benzyl-2:3-dihydro-1:3:4-thiodiazole gives a I_5 -, m.p. about 55—57°, and a I_3 -, m.p. about 85°, -derivative. The I_3 -derivatives with I- CHCl_3 yield the I_5 -derivatives. The fusion diagram of mixtures of (II) and (III) is given and confirms the individuality of the unstable I_5 -derivatives. Conversion of (II) into (III) is particularly facile, being achieved by washing (II) with CS_2 , or by repeatedly shaking an Et_2O suspension with a starch solution until no further blue colour is formed.

H. G. M.

(A) Cyanine dyes from amino-derivatives of benzthiazole. (B) Cyanine dyes from isomeric dimethylbenzthiazoles. A. I. KIPRIANOV and E. D. SITSCHEV (Trav. Inst. Chim. Charkov, 1936, 2, 15—24, 25—32).—(A) 5-Dimethylamino-1-methylbenzthiazole, m.p. 71°, prepared from 5-amino-1-methylbenzthiazole and *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_3\text{Me}$, or by a Berntsen synthesis from NPhMe_2 , yields a coloured 2-N- (I) and

a colourless 5-N-methiodide, both m.p. 250° (decomp.), and a 2-N- (II), m.p. 242°, and 5-N-ethiodide, m.p. 149°; the yield of 2-N-derivative rises with increasing duration and temp. of reaction with the alkyl iodides. 5-Diethylamino-1-methylbenzthiazole, b.p. 185—195°/15 mm. [2-N-ethiodide (III), m.p. 76°], was prepared analogously. In picoline (at the b.p.) $\text{CH}(\text{OEt})_3$ and (I) or (II) yield 5:5'-bis(dimethylamino)-2:2'-dimethyl- (IV), m.p. 244°, or -2:2'-diethyl-thiocarbocyanine iodide (V), and 5:5'-bis(diethylamino)-2:2'-diethylthiocarbocyanine iodide (VI) is prepared similarly from (III). The 8-Me derivative of (IV) is obtained when NMe_3 is added to the reaction mixture. The 8-Me derivatives of (V) and (VI) are prepared similarly to them, using $\text{CMe}(\text{OEt})_3$ in place of $\text{CH}(\text{OEt})_3$. 2-Iodoquinoline ethiodide and (I) in EtOH-KOH (1 hr. at the b.p.) yield 5-dimethylamino-1-methyl-2'-ethylthio- ψ -cyanine iodide, m.p. 171°, whilst with quinoline methiodide 5-dimethylamino-1':2-dimethylthioisocyanine iodide, m.p. 176°, is obtained. Max. light absorption data are recorded for the above dyes. The dyes are valuable sensitizers of photographic emulsions.

(B) Thiolacet-toluidide in aq. NaOH and aq. $\text{K}_3\text{Fe}(\text{CN})_6$ at 7° yield 1:3-dimethylbenzthiazole, b.p. 161—163°/55 mm., the ethiodide, m.p. 150°, of which gives 3:3'-dimethyl- or 3:3':8-trimethyl-2:2'-diethylthiocarbocyanine iodide when heated with $\text{CH}(\text{OEt})_3$ or $\text{CMe}(\text{OEt})_3$, respectively. 2-Amino-4-methylthiophenol and Ac_2O in C_6H_6 (at the b.p.; 2 hr.) yield 1:4-dimethylbenzthiazole, b.p. 153—156°/25 mm., m.p. 34°, from the ethiodide, m.p. 195—196°, of which are prepared 4:4'-dimethyl- and 4:4':8-trimethyl-2:2'-diethylthiocarbocyanine iodide. The sensitising action of the isomeric dyes is unaffected by position of the Me, but the greatest bathochromic effect is given by the 4:4'-Me₂ derivatives. R. T.

Isolation of erythroidine, an alkaloid of curare action, from *Erythrina americana*, Mill. K. FOLKERS and R. T. MAJOR (J. Amer. Chem. Soc., 1937, 59, 1580—1581).—The seeds of *E. americana* contain 0.7—0.9% of erythroidine, $\text{C}_{16}\text{H}_{19}\text{O}_3\text{N}$, m.p. 94—96° [hydrochloride, m.p. 228—229° (decomp.)], $[\alpha]_D^{25} +109.7^\circ$ in H_2O], which has curare action when administered orally or by injection.

R. S. C.

Lupin studies. XII. Alkaloids of *Lupinus laxus*, Rydb. J. F. COUCH (J. Amer. Chem. Soc., 1937, 59, 1469—1471; cf. A., 1936, 1131).—*L. laxus* contains sparteine, *d*-lupanine [di-*d*-camphor-sulphonate, m.p. 245—246.5° (corr.)], trilupine, and a small amount of a substance, $\text{C}_{15}\text{H}_{24}\text{O}_2\text{N}_2$, m.p. 176—177°, $[\alpha]_D^{25} +133.2^\circ$ in H_2O .

R. S. C.

Ergot alkaloids. XII. Synthesis of substances related to lysergic acid. W. A. JACOBS and R. G. GOULD, jun. (J. Biol. Chem., 1937, 120, 141—150).—A more detailed account of matter previously abstracted (this vol., 219). 3:4-Tri-methyleneindole, m.p. 58.5—59° (picrate, m.p. 164—166°), and 8-amino-1-hydroxymethyl-1:2:3:4-tetrahydronaphthalene, m.p. 111—112° (hydrochloride, picrate, m.p. 206—207°; N-Bz derivative, m.p. 195.5—197°), were also prepared by reduction (Na-BuOH) of Me 8-amino-1:2:3:4-tetrahydro-1-naphthoate (m.p. 75—76°). 3:1-NH₂-C₁₀H₆-CO₂H

was converted into 5:6-benzoquinoline-7-carboxylic acid, m.p. 298—300° [hydrochloride; 3'-NO₂-derivative, m.p. 310°; 3'-amino-lactam (formula, *loc. cit.*), m.p. 280° (hydrochloride; 1:2:3:4-H₄-derivative, m.p. 248—249°). This lactam was reduced (Na-BuOH) to the corresponding indole, named *ergoline*, m.p. 175—183° (hydrochloride), and 3'-amino-7-hydroxymethyl-1:2:3:4:7:8:9:10-octahydro-5:6-benzoquinoline, m.p. 80—85° (dihydrochloride).

F. R. G.

Strychnos alkaloids. XCIV. Oxidation of strychnine to monohydroxystrychnine, the so-called ψ -strychnine. H. LEUCHS (Ber., 1937, 70, [B], 1543—1547).—Examination of a series of strychnine (I) residues discloses the presence of monohydroxystrychnine (ψ -strychnine) (II). Since (II) is not present in technical (I) its origin lies in atm. oxidation. Preparatively (I) in CHCl₃ is exposed to air in the presence of N-NH₃ and Cu(OH)₂ and the product is treated with MeOH. After hydrolysis with 0.25N-HCl and addition of NaOAc a homogeneous material, m.p. 233°, [α]_D²⁰ +104°/d in CHCl₃, is obtained which is more or less rapidly (?) isomerised to (II), m.p. 263°, [α]_D²⁰ -129°/d in CHCl₃, by dissolution in N-HCl and reprecipitation from the hot solution by NH₃. Strychnine oxide appears to be formed also. H. W.

Strychnos alkaloids. XCV. Transformations of ψ -strychnine. H. LEUCHS, H. GRUNOW, and K. TESSMAR (Ber., 1937, 70, [B], 1701—1707; cf. this vol., 394).— ψ -Strychnine hydrochloride, whether crystallised from cold or hot solution, is C₂₁H₂₂O₅N₂·HCl·2H₂O, whereas the perchlorate is anhyd. if obtained from hot solution, whilst when crystallised from cold solution and then heated at 100° and 125°/15 mm. it is C₂₁H₂₀O₂N₂·HClO₄ (cf. Robinson and Blount, A., 1932, 1147). ψ -Strychnine Me ether with MeI affords the methiodide, m.p. 216°, of Robinson and Blount but the product does not contain OMe and hence is C₂₁H₂₂O₃N₂·MeI; it is accompanied by a (?) hydriodide, m.p. (indef.) 244°, which yields the base, C₂₂H₂₄O₃N₂ (I), when treated with NH₃. (I) is transformed by PhCHO and aq. KOH under relatively mild conditions into the *monobenzylidene* derivative, C₂₉H₂₈O₃N₂, m.p. 246—248° (vac.), and under more drastic conditions into the *dibenzylidene* compound, m.p. 284—286°, of Robinson and Blount. Hydrogenation (PtO₂) of C₂₂H₂₄O₃N₂ gives rapidly the base, C₂₂H₂₆O₃N₂, m.p. 293° (vac.) [perchlorate; CHPh derivative, m.p. 255—261° (vac.)]. Ring-fission of ψ -strychnine methiodide gives the *tert.* base, C₂₂H₂₆O₃N₂, m.p. 188—190° (vac.), which contains OMe and is hydrogenated to the *base*, C₂₃H₃₀O₃N₂ (II), m.p. 123—125° [CHPh derivative, m.p. 198—200° (vac.)]. Hydrolysis of (II) with 2N-HCl affords (I). ψ -Strychnine (III) gives a *benzylidene* derivative, isolated as the *Et* ether, C₃₀H₃₀O₃N₂, m.p. 202° or m.p. (vac.) 208—209°. Hydrogenation of (III) affords *dihydro- ψ -strychnine*, m.p. 130—135° (decomp.), [α]_D²⁰ +34.5°/d in CHCl₃ [Me ether, m.p. about 209° (decomp.), [α]_D²⁰ +75.7°/d in CHCl₃; NO-derivative, m.p. 228° (decomp.), [α]_D²⁰ +443°/d in CHCl₃]. H. W.

Berbine derivatives. V. Constitution of 8:9:16:17-tetrahydrocorydalinium salts. W.

AWE [with H. ETZRODT and H. UNGER] (Arch. Pharm., 1937, 275, 405—410; cf. this vol., 219).—Contrary to Gadamer (cf. A., 1911, i, 153), 8:9:16:17-tetrahydrocorydalinium iodide, decomp. from 225—230°, obtained from corydaline by I or Hg(OAc)₂ (identity of the product being confirmed by the absorption spectrum), with CH₂Ph·MgBr or MgPhBr gives 2:3:11:12-tetramethoxy-9-benzyl-16-methyl-16:17-didehydroberbine hydriodide, m.p. 186°, and 2:3:11:12-tetramethoxy-9-phenyl-16-methylberbine, m.p. 209°, respectively, the latter product being reduced by Zn-Cd-Hg in aq. HCO₂H to 9-phenylcorydaline. R. S. C.

Solanine-s. L. H. BRIGGS (J. Amer. Chem. Soc., 1937, 59, 1404—1405).—Solanine-s [nitrate, m.p. 296° (decomp.); hydriodide, m.p. 283—284° (decomp.); oxalate, m.p. 238° (decomp.); tartrate, m.p. 222° (decomp.)] has been isolated from *Solanum auriculatum* (cf. Oddo *et al.*, A., 1905, i, 455). The formula indicated by analysis, C₄₄H₇₅O₁₈N (solanidine-s, C₂₆H₄₃O₃N), is confirmed by the work of Rochelmeyer (this vol., 80), and differs only by H₂O from that of solanecarpine (Saiyed and Kanga, *ibid.*, 39), with which it appears to be identical. A. Lr.

Senecio alkaloids. IV. Alkaloids of *S. vulgaris*. Degradation of senecionine. L. KONVALOVA and A. ORÉKHOV (Bull. Soc. chim., 1937, [v], 4, 1285—1290; cf. A., 1935, 1387; 1936, 1277).—C₂H₄Cl₂ extracts senecionine (cf. A., 1936, 617, 1002) which with boiling N-NaOH gives senecic acid and retronecine (I), m.p. 120—121° (hydrochloride, m.p. 164—165°) (cf. A., 1935, 365). In N-HCl with H₂-Adams' catalyst (I) gives *retronecanol*, m.p. 98—99° [picrate, m.p. 210—211° (*lit.*, 208°); *picrolonate*, m.p. 184—185°] (cf. A., 1935, 365), which with conc. H₂SO₄ at 145—150° affords heliotridene, reduced (H₂-Adams' catalyst) to heliotridane. The chemical relationships of the *Senecio* and heliotrope alkaloids are discussed. J. L. D.

Sinomenine. XLV. Synthesis of N-methyltuduranine methyl ether. K. GOTO, R. INABA, and H. NOZAKI (Annalen, 1937, 530, 142—146; cf. A., 1936, 88).—2:4-NO₂·C₆H₃(OMe)·CH₂·CO₂H affords 2-nitro-4-methoxyphenylacetomoveratrylamide, m.p. 132°, converted by P₂O₅ in PhMe into 6:7-dimethoxy-1-2'-nitro-4'-methoxybenzyl-3:4-dihydroisoquinoline, m.p. 156° (84% yield), the methiodide of which with Zn dust and conc. HCl gives 6:7-dimethoxy-1-2'-amino-4'-methoxybenzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 102° (dihydrochloride, +0.5H₂O, m.p. 226°). With HNO₂, followed by Zn-HCl, this affords 3:5:6-trimethoxyaporphine hydrochloride, m.p. 245° (decomp.) (24% yield); resolution by tartaric acid gives the active bases, m.p. 108° after sintering at 100°, [α]_D²⁰ -136.94°, +138.16° in MeOH (l-base d-, m.p. 203—205°, and d-base l-tartrate, m.p. 204° after sintering at 200°); the l-base is identical with N-methyltuduranine Me ether, now obtained *cryst.* from tuduranine. Identity is confirmed by degradation of the *dl*-base to the same de-N-Me compound as is obtained from the natural l-compound. R. S. C.

Organo-arsenic compounds. IV. Heterocyclic ring containing arsenic. H. N. DAS-GUPTA

(J. Indian Chem. Soc., 1937, 14, 231—236).— $\text{CHCl}:\text{CH}:\text{AsCl}_2$ (I) heated with C_6H_6 with or without anhyd. AlCl_3 affords a mixture containing phenyl- β -chlorovinylchloroarsine (II), b.p. 138—142°/3 mm., and diphenyl- β -chlorovinylarsine (III), b.p. 190—198°/3 mm. (HgCl_2 derivative, m.p. 238°). MgPhBr converts (I) and (II) into (III). With AlCl_3 in CS_2 (II) affords 1-chloroarsindole, converted by MgMeI into 1-methylarsindole, b.p. 142—145°/6 mm. (methiodide, decomp. 216—218°; HgCl_2 derivative, m.p. 150—151°. The Cl-compounds are vesicants. P. G. C.

Composition of Grignard reagents as determined by precipitation with dioxan. C. R. NOLLER and W. R. WHITE (J. Amer. Chem. Soc., 1937, 59, 1354—1356).—Treatment of the Grignard solution 2MgRX (or $\text{Mg}_2\text{R}_2\text{X}_2$) $\rightleftharpoons \text{MgR}_2 + \text{MgX}_2$ with dioxan ppts. all but MgR_2 . If the mixture is shaken before separating the ppt., the proportion of MgR_2 left in solution rises rapidly to a const. val.; hence the method is useless for determining the composition of the original solution. Addition of MgR_2 or MgX_2 to such a solution has little effect on the composition of the ppt. A. LI.

4:4'-Organo-magnesium derivatives of diphenyl. Catalytic action of magnesium iodide. R. GIBERT (Compt. rend., 1937, 205, 443—445; cf. A., 1934, 880).—4:4'-Di-iodo- and -bromodiphenyl and Mg afford the Mg_2 derivative (no Mg_1 derivative was formed), reacting normally with H_2O and with PhCN , and with COPh , to give 4:4'-di(hydroxydiphenylmethyl)diphenyl (cf. A., 1907, i, 503) and a substance, m.p. 216°. The yield of Mg_2 compounds is increased by adding Mg halide (cf. A., 1934, 397). J. L. D.

Action of bromine on proteins. F. LIEBEN and R. TANDLER [with P. WEISS] (Biochem. Z., 1937, 292, 82—91; cf. A., 1928, 1388).—In brominated caseinogen Br is much more firmly bound than in brominated collagen and gelatin. In brominated proteins Br is very probably not attached to the rings of cyclic NH_2 -acid residues. W. McC.

Structure of protein monolayers.—See A., I, 511.

Protein films.—See A., I, 511.

Cryolysis of casein.—See A., I, 515.

Chondroitinsulphuric acid.—See A., III, 340.

Free amino- and carboxyl groups in proteins.—See A., III, 340.

Photosynthetic melanins.—See A., III, 374.

Determination of [amino-acid] coefficient D .—See A., III, 374.

Crystalline protein with high lactogenic activity.—See A., III, 375.

Manometric determination of volatile substances soluble in water with special reference to ether. M. JOWETT (Biochem. J., 1937, 31, 1097—1100).—The application of a const.-vol. manometer to the determination of volatile gases and liquids sol. in H_2O , the partition of which between aq. and gaseous phases varies considerably with temp., is described. F. O. H.

Volumetric micro-determination of oxygen (ter Meulen procedure). (MLLE.) A. LACOURT (Compt. rend., 1937, 205, 280—282).—The O is converted into H_2O and this acts on cinnamoyl chloride, liberating HCl which is titrated. A precision of $\pm 0.3\%$ on quantities of 3—5 mg. can be obtained. F. J. G.

Determination of organic halogen compounds in presence of free sulphur. C. B. MEDINSKI and I. V. KOSTROV (Zavod. Lab., 1937, 6, 696—698).—A modified Dennstedt apparatus is described. R. T.

Analysis of nitrogenous organic compounds. II. General method of detection of nitrogen. Z. E. GOLBRAICH (J. Appl. Chem. Russ., 1937, 10, 1135—1139).—The substance is heated with MnO_2 , and the combustion gases are absorbed in H_2O , to which Griess-Ilosvay reagent is then added; a red coloration indicates N. In the case of inorg. compounds addition of sugar is recommended. R. T.

Analytical uses of Nessler's reagent. III. Determination of formaldehyde, pyrogallol, tannic and gallic acids; their absolute oxygen values. M. GOSWAMI and A. SHAHA (J. Indian Chem. Soc., 1937, 14, 208—231).— CH_2O , pyrogallol (in absence of O_2), tannic and gallic acids can be micro-determined by treating with Nessler's reagent, dissolving the pptd. Hg in standard I solution, and titrating with $\text{Na}_2\text{S}_2\text{O}_3$. P. G. C.

Electrotitration of acids in benzene solution.—See A., I, 529.

3:5-Dinitro-*p*-toluic acid as a reagent for the identification of amines. P. P. T. SAH and K. H. YUIN (J. Chinese Chem. Soc., 1937, 5, 129—133).—The 3:5-dinitro-*p*-toluates of the following amines are suitable for identification purposes: NH_2Ph , m.p. 159—160°, *o*-, m.p. 146—147°, *m*-, m.p. 128—129°, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 157—159°, α -, m.p. 137—138°, and β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. 112—113°, *o*-, m.p. 188—189°, and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, m.p. 207—208°, *p*-aminodiphenyl, m.p. 178—179°, benzidine, m.p. 231—232°, $\text{C}_6\text{H}_5\text{N}$, m.p. 150—151°, quinoline, m.p. 149—151°, *o*-, m.p. 142—143°, and *p*-toluquinoline, m.p. 155—156°, quinaldine, m.p. 121—122°, *p*-toluquinoline, m.p. 122—123°, NH_3 , m.p. 226—228°, NH_2Me , m.p. 206—207°, $\text{CO}(\text{NH}_2)_2$, m.p. 137—138°, *p*-xylydine, m.p. 162—163°, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, m.p. 164—165°, *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, m.p. 119—120°, and *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 214—216°. F. R. S.

Determination of proline in protein hydrolysates.—See A., III, 374.

Leuco-bases as analytical reagents. A. IONESCO-MATIU and C. POPESCO (Bull. Soc. chim., 1937, [v], 4, 1230—1235).—Methylene-blue and $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of HCl give a leuco-base (I), stable in air for 12 hr. Nascent H, NaHS , Na_2SO_3 , NaHSO_3 , and $\text{Na}_2\text{S}_2\text{O}_5$ do not stabilise (I). Neutral salts, except Hg^{++} , Cu^{++} , etc. salts, do not, and only aldehydes amongst many org. substances, affect (I). Oxidation to the coloured form is facilitated by light. Stabilisation of (I) by $\text{Na}_2\text{S}_2\text{O}_4$ may be due to the formation of an $\text{S}\cdot\text{SO}_3\text{H}$ derivative (cf. A., 1911, i, 1006). J. L. D.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1937.



Recent investigations on thermal changes in simple organic compounds. M. W. TRAVERS (Trans. Faraday Soc., 1937, 33, 1342—1353).—The results of recent studies of the thermal decomp. of MeCHO, simple hydrocarbons, $(CH_3)_2O + MeCHO$, NH_2Me , ethers, and alkyl nitrites, and the conclusions reached from them, are discussed. For such reactions the determination of order of reaction from the half-life period is impossible. The importance of the initial stages of the reaction is emphasised.

J. W. S.

Structure of aliphatic compounds: Walden inversion. W. TAYLOR (Rec. trav. chim., 1937, 56, 898—899; cf. A., 1, 417).—In simple reactions (e.g., hydrolysis and esterification) of Me, Et, Pr^i , and Bu^i compounds, the high relative speed of reaction of Bu^i is interpreted by assuming that in primary and sec. aliphatic compounds, RX, X is partly bound by the α -H. This view conforms with the theories of Polanyi and others to account for the Walden inversion.

F. L. U.

Mechanism of the reaction of substitution and Walden inversion. P. A. LEVENE, A. ROTHEN, and M. KUNA (J. Biol. Chem., 1937, 120, 777—797).—It is shown that in normal saturated aliphatic derivatives, substitution on the asymmetric C by a negative group or atom is connected with an inversion of configuration. In substances $CHRR'X$ when $R = \cdot CH_2CH_3$, substitution of a N_3 group for halogen proceeds without inversion of configuration, whilst when $R' = Ph$ substitution of Br for OH by HBr or PBr_3 in absence of C_5H_5N takes place without inversion of configuration, but in presence of C_5H_5N with inversion. For normal, saturated alkyl derivatives substitution is connected with inversion provided the mechanism of substitution of N_3 for halogen proceeds by the same mechanism as the substitution of one halogen for another. A general theory of the Walden inversion is not yet possible. d- δ -Chloro-octane, b.p. $92^\circ/50$ mm., $d_{25}^{25} +0.28^\circ$ ($l = 1$), and d- γ -chloro-octane, b.p. $98^\circ/33$ mm., $\alpha_D^{25} +5.10^\circ$ ($l = 1$), are obtained from the requisite I-compound and LiCl in MeOH at 37° . Δ^a -Hepten- γ -ol, b.p. 103 — $106^\circ/147$ mm., $[\alpha]_D^{25} -23.2^\circ$, and PCl_5 in dry Et_2O give d- γ -chloro- Δ^a -heptene (I), b.p. 92 — $94^\circ/125$ mm., $[\alpha]_D^{25} +9.76^\circ$, converted by NaN_3 in H_2O -MeOH at 25° into γ -azido- Δ^a -heptene, b.p. 78 — $81^\circ/32$ mm., $[\alpha]_D^{27} -0.04^\circ$, reduced (Adams) to l- γ -aminoheptane, b.p. 100 — $106^\circ/148$ mm., $[\alpha]_D^{27} -0.02^\circ$; another sample of the latter substance, b.p. 99 — $101^\circ/150$ mm., $[\alpha]_D^{27} -0.45^\circ$, was obtained by hydrogenating (Adams) l- γ -amino- Δ^a -heptene, b.p. 95 — $105^\circ/155$ mm., $\alpha_D^{23} -4.80^\circ$ ($l = 1$), derived, with

a sec. amine, b.p. 92 — $95^\circ/1$ mm., $[\alpha]_D^{25} +0.52^\circ$ ($l = 1$), from (I) in NH_3 -MeOH at 25° and then at 50° . l- γ -Bromo- Δ^a -heptene, b.p. 92 — $94^\circ/50$ mm., $[\alpha]_D^{25} -4.64^\circ$, is converted by LiCl in MeOH at 25° into d- γ -chloro- Δ^a -heptene, b.p. 87 — $88^\circ/90$ mm., $[\alpha]_D^{25} +0.90^\circ$. r- α -Phenylethan- α -ol is converted into the H phthalate, m.p. 108° , from which, after resolution with brucine, l- α -phenylethan- α -ol, b.p. $75^\circ/1$ mm., $[\alpha]_D^{25} -42.0^\circ$, is obtained. This is converted by $SOCl_2$ into l- α -chloro- α -phenylethane, b.p. $101^\circ/50$ mm., $[\alpha]_D^{25} -24.0^\circ$, whence successively d- α -azido- α -phenylethane, b.p. $114^\circ/50$ mm., $[\alpha]_D^{25} +18.6^\circ$, and d- α -amino- α -phenylethane, b.p. $75^\circ/15$ mm., $[\alpha]_D^{25} +3.14^\circ$. l- α -Phenylpropan- α -ol (II), b.p. 94 — $95^\circ/10$ mm., $[\alpha]_D^{25} -22.2^\circ$ (obtained by resolving the r-alcohol through the strychnine phthalate), and $SOCl_2$ afford l- α -chloro- α -phenylpropane, b.p. 77 — $80^\circ/10$ mm., $[\alpha]_D^{25} -28.9^\circ$, whence d- α -azido- α -phenylpropane, b.p. 100 — $101^\circ/22$ mm., $\alpha_D^{25} +32.95^\circ$ ($l = 1$), and d- α -amino- α -phenylpropane, b.p. $81^\circ/10$ mm., $[\alpha]_D^{25} +4.57^\circ$. PBr_5 and (II) in C_5H_5N give l- α -bromo- α -phenylpropane, b.p. 57 — $61^\circ/0.6$ mm., $\alpha_D^{25} -47.7^\circ$, converted by 40% NH_3 -MeOH into the amine, b.p. 88 — $90^\circ/16$ mm., $[\alpha]_D^{25} +3.65^\circ$. l- α -Phenylbutan- α -ol, b.p. 121 — $123^\circ/18$ mm., $[\alpha]_D^{25} -7.62^\circ$ [hydrogenated (Adams) to l- α -cyclohexylbutyl- α -ol, b.p. 76 — $77^\circ/1.5$ mm., $[\alpha]_D^{25} -4.61^\circ$], is converted by PBr_5 in $CHCl_3$ - C_5H_5N into d- α -bromo- α -phenylbutane, b.p. 67 — $75^\circ/0.5$ — 1 mm., $[\alpha]_D^{25} -17.6^\circ$, and by PBr_5 in $CHCl_3$ into l- α -bromo- α -phenylbutane, b.p. 67 — $72^\circ/0.5$ — 1 mm., $[\alpha]_D^{25} -1.98^\circ$, whereas the alcohol and PBr_5 gave a sample of b.p. 65 — $72^\circ/0.5$ — 1 mm., $[\alpha]_D^{25} -0.20^\circ$. PCl_5 and the alcohol gave a hydrocarbon, $C_{10}H_{12}$, b.p. 147 — $152^\circ/1.5$ mm. Inversion occurs during the transformation of the bromide into the chloride by LiCl. l- α -Amino- α -phenylbutane has b.p. $105^\circ/10$ mm., $[\alpha]_D^{25} -2.28^\circ$ (hydrochloride, $[\alpha]_D^{25} +0.66^\circ$ in H_2O), if derived from l- α -azido- α -phenylbutane, b.p. 85 — $90^\circ/4$ mm., $[\alpha]_D^{25} -16.4^\circ$, but b.p. 103 — $104^\circ/15$ mm., $[\alpha]_D^{25} -0.83^\circ$, when obtained from the bromide and NH_3 .

H. W.

Catalytic isomerisation of n- and iso-butane. C. W. MONTGOMERY, J. H. McATEER, and N. W. FRANKE (J. Amer. Chem. Soc., 1937, 59, 1768—1769).—5% of $AlBr_3$ equilibrates n- and iso- C_4H_{10} , giving about 20% of the former; as by-products only 2—3% of CH_4 and C_2H_6 are formed.

R. S. C.

Synthesis of branched hydrocarbons with long chains. K. H. MEYER and P. STREULI (Helv. Chim. Acta, 1937, 20, 1179—1183).—Octadecyl alcohol is converted by PCl_5 into octadecyl chloride, m.p. 18° , and by HBr at 150° into the corresponding

bromide, m.p. 41°, neither of which reacts with Mg. *Octadecyl benzoate*, m.p. 42°, decomposes at 300° into BzOH and *octadecene*, b.p. 179—180°/18 mm., m.p. 18°, the dibromide, m.p. 22°, of which is transformed by KOH at 270°/0.1 mm. into Δ^{α} -*octadecinenene* (I), m.p. 28° (*Ag* derivative and salt $C_{16}H_{33}Cl \cdot AgNO_3$, which when heated in xylene gives Δ^{α} -*hexatriacontadinenene*, m.p. 59°). Reaction does not occur between MgMeI in boiling Et_2O , whereas CH_4 is evolved from solution in boiling Bu_2O , but the Grignard compound (II) does not react with PhCHO, BzCl, MeOBz, $AsCl_3$, $SiCl_4$, or thapsonitrile (III) and is not hydrogenated (Pt). With CO_2 it affords Δ^{α} -*nonadecinenic acid*, m.p. 59.5°, in 25% yield and with $COPh_2$ it gives α -*hydroxy- α -diphenyl- Δ^{β} -nonadecinenene*, m.p. 54°. Treatment of (III) with MgEtI in Et_2O-Bu_2O at 60° affords *eicosane- γ -dione*, m.p. 93°, converted by (II) into 19:34-*dihydroxy-19:34-diethyl- $\Delta^{17,35}$ -dopentacontadi-ene*, $C_{14}H_{28}[C(Et)(OH) \cdot C \cdot C \cdot C_{16}H_{33}]_2$, m.p. 42° (yield 88%), reduced to 19:34-*diethylidopentacane*, m.p. 26°.

H. W.

Ratio of substitution in addition in the reaction of chlorine with olefines in dilute carbon tetrachloride solution. T. D. STEWART, K. DOD, and G. STENMARK (J. Amer. Chem. Soc., 1937, 59, 1765—1766).—Rates of reaction with Cl_2 in CCl_4 are Δ^{β} - $C_5H_{10} > \Delta^{\gamma}$ - $C_7H_{14} > \Delta^{\beta}$ - $C_6H_{12} > \Delta^{\delta}$ - $C_7H_{14} \gg \Delta^{\alpha}$ - $C_5H_{10} > \Delta^{\alpha}$ - C_7H_{14} . The ratio of addition to substitution is determined for these olefines. Excess of olefine or Cl_2 increases and decreases, respectively, substitution. With Δ^{α} - C_5H_{10} increase in concn. increases substitution, but with C_7H_{14} decreases it.

R. S. C.

Catalytic polymerisation of ethylene at atmospheric pressure. III—V. Y. KONAKA (J. Soc. Chem. Ind. Japan, 1937, 40, 236—237B; cf. this vol., 43).—III. The Co catalyst is improved by the addition of 20% of Cu to Ag. The influence of a no. of metallic oxides and salts has been examined.

IV. The Co-Ag catalyst is best prepared by pptg. the nitrates with K_2CO_3 followed by reduction at 350°. A good catalyst is given by Co-Ag- U_3O_8 -kieselguhr (10:2:2:12).

V. The optimum temp. (290—300°) varies slightly with the catalyst used and the rate of flow of the C_2H_4 has a considerable influence on the yield of liquid polymeride.

F. R. G.

Gaseous polymerisations.—See A., I, 569.

Isomeric Δ^{β} -pentenes. H. J. LUCAS and A. N. PRATER (J. Amer. Chem. Soc., 1937, 59, 1682—1686).—The hydriodides, m.p. 42—42.5° and an oil, respectively of *trans*-, b.p. 106.5°/10 mm., m.p. 24.1°, n_D^{25} 1.4578 (*p*-phenylphenacyl ester, m.p. 90—91°; dibromide, m.p. 97—98°), and *cis*- α -methyl- Δ^{α} -pentenoic acid, b.p. 94—94.4°/10 mm., m.p. —42°, n_D^{25} 1.4488 (dibromide, an oil; *p*-phenylphenacyl ester, m.p. 44.5—45.8°) (prep. from $OH \cdot CMePr \cdot CO_2H$), with aq. $NaHCO_3$ give pure *trans*- (I), b.p. 36.2°, f.p. —180° to —178°, n_D^{25} 1.3817, and nearly pure *cis*- Δ^{β} -pentene (II), b.p. 36.2°, f.p. —135° to —136°, n_D^{25} 1.3799, which afford the dibromides, b.p. 91°/50.1 and 92.4°/50.1 mm., f.p. —55° to —53° and —44° to —41°, n_D^{25} 1.5096 (both), d_4^{20} 1.6809 and 1.6817, respectively, and with HBr bromopentenes, b.p. 117.5° and 116.5—

118.5°, n_D^{25} 1.4435 and (?) 1.4425, respectively. The properties of pentenes prepared by other investigators are considered in the light of these data; many samples were mixtures. The experimental basis of the hypothesis of electronic isomerism of olefines is removed.

R. S. C.

Constitution of lycopene. R. KUHN and C. GRUNDMANN (Ber., 1937, 70, [B], 1905—1906).—In reply to Karrer and Solmssen (this vol., 378) it is pointed out that the authors' conclusions with regard to the formula of lycopene are independent of the yields of methylheptenone and the dialdehyde $C_{24}H_{28}O_2$ obtained by its oxidation (A., 1932, 749).

H. W.

Hydrogenation of acetylene and ethylene with palladium as catalyst.—See A., I, 524.

Hydrogenation of acetylene to ethylene. P. ACKERMANN (Brennstoff-Chem., 1937, 18, 357—361).

—By passing mixtures of C_2H_2 with excess of H_2 over Ni-kieselguhr at 80—150°, using narrow tubes and a short layer of catalyst, up to 70% of the C_2H_2 is converted into C_2H_4 . C_2H_6 and liquid polymerides are also formed. The formation of C_2H_6 is diminished by using narrow tubes having their inner surface coated with a thin layer of catalyst, or Ni tubes the surface of which has been activated. By hydrogenation in the liquid phase even at relatively low temp. some polymerides are formed.

A. B. M.

The "peroxide" or "oxygen" effect. J. C. SMITH (Chem. and Ind., 1937, 833—839).—A review of the available data on the effect of O_2 and peroxides on the addition of H halides to unsaturated compounds.

J. D. R.

Kinetics and mechanism of polymerisation processes. S. MEDVEDEV (Prom. Org. Chim., 1937, 3, 472—481).—Polymerisation of $CH_2 \cdot CCl \cdot CH \cdot CH_2$ consists in aggregation of the active units $\cdot CH_2 \cdot CCl \cdot CH \cdot CH_2 \cdot$ (I), to yield chains, followed by development of units of the type $\cdot CH_2 \cdot CCl \cdot CH \cdot CH_2 \cdot$ (II) in the straight-chain polymeride, to yield branched chains and rings. Approx. expressions are derived for velocity of polymerisation; the exact equations cannot be derived, owing to differences in the probability of attachment of (I) to (II) units, according to whether the latter are situated at the surface or near the centre of an aggregate. It is shown that the velocity rises with increasing concn. of monomeride, to a limiting val. determined by the free surface of the polymeride.

R. T.

Synthesis of polychloro-compounds by aluminium chloride. IV. **Condensation of hexachloropropylene with *s*-dichloroethylene.** H. J. PRINS (Rec. trav. chim., 1937, 56, 779—784; cf. this vol., 174).— $CCl_3 \cdot CCl \cdot CCl_2$ and $AlCl_3$ at 80° form a cryst. additive compound, which reacts vigorously with $(CHCl)_2$, but the only product isolated was a compound, $C_3H_5Cl_{11}$, m.p. 113—114°, b.p. 190°/2 mm., formed by reaction of 3 mols. of $(CHCl)_2$. Cautious reaction in CH_2Cl_2 at 5—6° affords a good yield of $\alpha\beta\gamma\delta\epsilon$ -*octachloro- Δ^{α} -pentene*, b.p. 113—113.5°/2 mm., which with $\approx 96\%$ H_2SO_4 gives SO_3 , HCl, $\alpha\beta\gamma\delta\delta$ -*penta-chloro*[(?)- Δ^{α}]-*pentenoic acid*, m.p. 120—124.5° (loses

1 HCl to KOH-EtOH), and an isomeric acid, m.p. 133—136.5°. Both acids lose 4—5 Cl to Na₂CO₃.

R. S. C.

Kinetics of the synthesis of methyl alcohol.—See A., I, 525.

Heterogeneous catalytic racemisation of *l*-isobutyl alcohol.—See A., I, 573.

Synthesis of a glycerol-*d*₁ from optically active isopropylidene-*d*-glyceraldehyde. H. ERLÉNMEYER, H. O. L. FISCHER, and E. BAER (Helv. Chim. Acta, 1937, 20, 1012—1014).—Treatment of isopropylidene-*d*-glyceraldehyde in EtOAc containing D₂O and Ni (Rupe) with D₂ gives *d*-isopropylidene-glycerol-*d*, C₅H₉O₂·CH_{1.62}D_{1.38}O, b.p. 78.5—79.5°/11 mm., [α]_D²⁰ +11.8°, whence glycerol-*d*, C₂H₅O₂·CH_{2.1}D_{0.9}O, b.p. 165—166°/12 mm., [α]_D²⁰ 0.00±0.01°. H. W.

Naturally occurring monoanhydrohexitols. W. FREUDENBERG and E. F. ROGERS (J. Amer. Chem. Soc., 1937, 59, 1602—1605).—Styracitol, m.p. 155°, [α]_D²⁵ -48.5° in H₂O, [α]_D²⁵ -50.5° in aq. H₃BO₃, is oxidised by Pb(OAc)₄ more rapidly than is polygalitol (I), m.p. 142—143°, [α]_D²⁵ +42.86° in H₂O, [α]_D²⁵ +45° in aq. H₃BO₃ (prep. from *Polygala senega* in 0.22% yield). The former is thus α₆-anhydromannitol and the latter α₆-anhydrosorbitol, configurations which are confirmed by consideration of optical superposition. Aceritol and (I) are identical. Hydrogenation (Pd-black) of oxygalactal tetraacetate, freed from (?) β-*d*-galactose 2:3:4:6-tetraacetate by crystallisation, gives α₆-anhydrodulcitol [(?) -talitol] tetraacetate, m.p. 108°, [α]_D²⁵ -15.31° in CHCl₃, hydrolysed by Ba(OH)₂ to α₆-anhydrodulcitol [(?) -talitol], a syrup, [α]_D²⁵ -7.34° in H₂O. R. S. C.

Synthesis of glycerides. II. P. E. VERKADE, J. VAN DER LEE, J. C. DE QUANT, and E. DE ROY VAN ZUYDEWIJN (Proc. K. Akad. Wetensch. Amsterdam, 1937, 40, 580—583; cf. A., 1935, 326).—In glycerides of the type OR·CH(CH₂·O·CPh₃)₂ (I) and CPh₃·O·CH₂·CH(OR)·CH₂·OR' (II) (R, R' is acyl), the CPh₃ may be removed by H₂-Pd in EtOH without wandering of the acyl groups. On the basis of this and lit. data on the wandering of acyl groups in the hydrolysis of CPh₃ from glycerides of the type (I) and (II) with acid, the following general method for the synthesis of glyceryl esters is outlined. Reduction of (I) or (II) with H₂-Pd in EtOH affords β-glycerides and βγ-diglycerides, respectively; fission of (II) with HCl yields αγ-diglycerides of known structure. The βγ- and αγ-diglycerides with R''Cl and C₅H₅N afford triglycerides containing three different acyl groups and of definite structure. J. D. R.

Reduction of glycerides by Bouveault and Blanc's method. V. M. MITCHOVITCH and G. STEFANOVITCH (Compt. rend., 1937, 205, 386—388).—Interaction of olein and palmitin with Na in boiling EtOH, BuⁿOH, or amyl alcohol affords oleyl and cetyl alcohol. Similarly, olive oil, lard, cod-liver oil, and chaulmoogra oil afford mixtures of alcohols.

J. L. D.

Glycerides of elaidic acid. A. BÖMER and W. KAPPELLER (Fette u. Seifen, 1937, 44, 340—343).—

The elaidoglycerides α-palmito-β'-dielaidin, m.p. 46.3°, α-stearyl-β'-dielaidin, m.p. 49.9°, α-elaido-β'-dipalmitin, m.p. 51.7°, α-elaido-β'-distearin, m.p. 60.7°, and trielaidin, m.p. 40.7°, have been synthesised from glycerol and the respective acids. E. L.

Fission of Robison's ester by triphosphopyridine nucleotide. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1937, 292, 287—295).—Phosphohexonic acid (Robison and King, A., 1931, 523) is oxidised by systems containing the nucleotide and protein intermediary enzymes I and II (Negelein and Gerischer, A., 1936, 638), the oxidation being more complete in the presence of glucose or, to a greater extent, fructose. The end products include two esters with C:P = 3:1 and 6:1, respectively.

F. O. H.

Preparation of esters from alcohols and acid chlorides in the presence of magnesium. Esterification of tertiary alcohols. A. SPASSOV (Ber., 1937, 70, [B], 1926—1930).—A solution of the acid chloride in Et₂O is gradually added to the carbinol in Et₂O containing Mg powder. Reaction is usually vigorous and after about 1 hr. at room temp. is completed during 2 hr. on the water-bath, after which the product is cooled, treated with dil. NaHCO₃, and the ester is extracted with Et₂O. The change is CR₃·OH + R'·COCl = OH·CR'Cl·O·CR₃ (I); (I) = R'CO₂CR₃ + HCl; Mg + 2HCl = MgCl₂ + H₂. In addition to reacting with HCl, the Mg has a secondary action, since it cannot be replaced by Fe, Al, or Zn. This sp. action is obvious in the acceleration of esterification and the suppression of the dehydrating action of the acid chloride on the *tert.* alcohol. BuⁿOH, CMe₂Et·OH, CMeEt₂·OH, and CEt₃·OH are smoothly and rapidly acylated, the yield being >60%. CPh₃·OH could not be thus esterified, but C(CH₂Ph)₃·OH gives a 50% yield of ester. AcCl, EtCOCl, PrCOCl, and PrⁱCOCl react readily with primary, *sec.*, and *tert.* alcohols (yields 50—90%). CH₂Ph·COCl reacts readily with BuⁿOH, but with BzCl the reaction proceeds less favourably. The following appear new: trimethylcarbinyl propionate, b.p. 115—116.5°, and phenylacetate, b.p. 114—117°/14 mm.; dimethylethylcarbinyl propionate, b.p. 153—156°/710 mm.; tribenzylcarbinyl acetate, m.p. 80—81°; triethylcarbinyl butyrate, b.p. 83—86°/13 mm., and phenylacetate, b.p. 142—146°/13 mm. H. W.

Replacement series of alkyl groups as determined by alcoholysis of esters. II. G. B. HATCH and H. ADKINS (J. Amer. Chem. Soc., 1937, 59, 1694—1696; cf. A., 1935, 472).—The equilibrium ratios, ROAc/ROMe, obtained in the reaction ROAc + MeOH ⇌ ROH + MeOAc, at 200° (actually measured for reaction of EtOAc and calc. for MeOAc), are R = Et 0.81, Pr^a 0.79, Bu^a 0.80, *n*-amyl 0.98, -hexyl 0.88, -nonyl, and -decyl 0.88, -octyl 0.85, and -dodecyl 0.84, Prⁱ 0.55, *sec.*-Bu 0.53, CHMePr^a 0.80, CHMeBu 0.7, CHMe·C₅H₁₁ 0.71, CHMe·C₆H₁₃ 0.68, CHMe·C₇H₁₅ 0.63, Buⁱ 0.66, CH₂·CHEt₂ 0.92, CH₂·CHEtBu^a 1.01, CHMeBuⁱ 0.72, cyclohexyl 0.57, allyl 0.62, benzyl 0.59, CH₂Ph·CH₂ 0.63, Ph·[CH₂]₃ 0.83. Substitution by Me or unsaturated residues reduces the ratio, unless Me is sterically near O. R. S. C.

Thermal transformations of potassium and sodium formate in presence of alkali hydroxides.—See A., I, 523.

Hydrolysis of acid chlorides. IV.—See A., I, 571.

Basic lead acetates. R. DUBRISAY and A. SAINT-MAXEN (Compt. rend., 1937, 205, 325—326; cf. A., 1936, 1464).—Addition of aq. NH_3 in increasing amounts to solutions of neutral $\text{Pb}(\text{OAc})_2$ does not alter the ultra-violet absorption spectrum, in which there is no definite band until the mixture, which contains two basic Pb acetates, contains 0.5 g.-mol. of NH_3 and 1 g.-mol. of Pb. With higher concns. of NH_3 , the spectrum is altered. The X-ray diffraction spectrum of the more sol. compound is identical with that of Plöchl's compound, $\text{Pb}_2(\text{OAc})_3 \cdot \text{OH}$. The less sol. exhibits a characteristic X-ray spectrum which indicates that it is not a mixture and is not hydrocerusite. J. L. D.

Hydration of acetylenes. I. Δ^0 -Undecynoic acid (undecolic acid). (Miss) M. L. SHERRILL and J. C. SMITH (J.C.S., 1937, 1501—1503).—Hydration of Δ^0 -undecynoic acid with H_2SO_4 yields 59% of 0- and 41% of α -ketoundecolic acid, whilst with $\text{Hg}(\text{OAc})_2$ the respective proportions formed are 46% and 54%. J. D. R.

Exchange reaction of organic compounds with D_2SO_4 . R. SCHOENHEIMER, D. RITTENBERG, and A. S. KESTON (J. Amer. Chem. Soc., 1937, 59, 1765).—D has been introduced into palmitic acid, *dl*-alanine, *d*-leucine (I), and cholesteryl chloride dibromide by exchange with D_2SO_4 in H_2SO_4 . (I) was racemised. E. S. H.

Kolbe electrosynthesis of several organic acids. S. KITaura (Bull. Inst. Phys. Res. Japan, 1937, 16, 765—772).—Kolbe electrolysis of oleic, ricinoleic, palmitic + phenylacetic, and palmitic + β -phenylpropionic acids gives tetratriacontadiene, the glycol $(\text{CH}_2)_{14}[\text{CH}:\text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot (\text{CH}_2)_5\text{Me}]_2$, cetylbenzene, and heptadecylbenzene, respectively. E. W. W.

Isomerides formed in the course of the hydrogenation of erucic acid. Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1937, 40, 283—285B).—Et erucate is hydrogenated (Ni-kieselguhr at 180—185°) to a product hydrolysed to a mixture containing behenic (I) and brassidic (II) acid, and other isomerides of erucic acid. Products of oxidation (KMnO_4) of the mixed Et esters from (I), (II), and (III) suggest that the Δ^u -ethylenic linking has migrated partly to the Δ^u - and partly to the Δ^s - and perhaps the Δ^o -positions. E. W. W.

Optical activity of lactic acid produced by *Lactobacillus acidophilus* and *L. bulgaricus*.—See A., III, 316.

Specificity of the salicylaldehyde reaction [for pyruvic acid] of Csonka-Straub. A. E. BRAUNSTEIN (Nature, 1937, 140, 427).—The reaction is positive with all compounds containing Ac linked directly to H or C. It is negative with O- and N-Ac compounds, the CO of which is not a genuine carbonyl group. The mechanism of the reaction is discussed, and the need for care in its application to quant.

investigations on the metabolism of AcCO_2H emphasised. L. S. T.

Ethyl acetoacetate and metallic copper. B. CROCCA (Gazzetta, 1937, 67, 346—351).—In presence of air, Cu reacts slowly with $\text{CH}_3\text{Ac} \cdot \text{CO}_2\text{Et}$ (I) at 50—60° to give the Cu derivative of (I), also obtained from Cu_2O , or from CuO that has not been strongly heated. Cu reacts similarly with CH_2BzAc or with CH_2Ac_2 , but not with COMe_2 , COMeEt , or COPh_2 . E. W. W.

Peroxide effect in the rearrangement of α -bromoacetoacetic ester. M. S. KHARASCH, E. STERNFELD, and F. R. MAYO (J. Amer. Chem. Soc., 1937, 59, 1655—1657).— $\text{CHAcBr} \cdot \text{CO}_2\text{Et}$ and $\text{CMeAcBr} \cdot \text{CO}_2\text{Et}$ rearrange to γ -Br-esters in the absence of light and air only if HBr and a peroxide (ascarirole) are present; HBr or a peroxide alone is ineffective. As normally prepared $\text{CHAcBr} \cdot \text{CO}_2\text{Et}$ is slowly rearranged by HBr in vac., but this is due to traces of peroxide present, since prep. in H_2 usually gives a stable α -Br-ester. Light accelerates the change by HBr. HCl does not effect rearrangement. The peroxide effect is due to a chain mechanism involving liberation of Br atoms from HBr by a peroxide and/or O_2 . R. S. C.

Paramagnetic isomerisation of maleic acid into fumaric acid.—See A., I, 573.

Ozonisation of maleic anhydride. Production of a very explosive ozonide. E. BRINER and D. FRANK (Helv. Chim. Acta, 1937, 20, 1211—1213).—Ozonisation of maleic anhydride in CHCl_3 or EtCl at -60° to -80° gives a particularly unstable and explosive ozonide. According to the quantity of O_3 absorbed it has the composition $(\text{CH} \cdot \text{CO})_2\text{O} \cdot \text{xO}_3$. H. W.

Enzymic hydrogenation of fumaric acid.—See A., III, 392.

Synthesis of *trans-trans*-muconic acid from fumaric acid. H. ERLÉNMEYER and W. SCHOENAUER (Helv. Chim. Acta, 1937, 20, 1008—1012).—Me H fumarate is converted by SOCl_2 into the corresponding chloride, b.p. 70—71°/14 mm., m.p. 16°, converted by 5% H_2O_2 in presence of $\text{C}_5\text{H}_5\text{N}$ into the peroxide, decomp. 129°. This passes when heated mainly into Me_2 *trans-trans*-muconate, m.p. 158°, but a more fundamental reaction resulting in the evolution of C_2H_2 also occurs. H. W.

Synthesis of Hildebrandt's acid; synthesis of methylated polyenedicarboxylic acids. R. KUHN and C. GRUNDMANN (Ber., 1937, 70, [B], 1894—1904).— Bu^uCHO , obtained by oxidising *n*-amyl alcohol with $\text{Na}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 at 100°, is brominated at -20° to -15° in CHCl_3 in strong light and then converted by EtOH into α -bromo-*n*-valeraldehyde *Et}_2* acetal, b.p. 92—96°/12 mm. This is transformed by solid KOH at 150° into Δ^u -pentenal *Et}_2* acetal, b.p. 163—165°, hydrolysed by 2N- H_2SO_4 to Δ^u -pentenal, b.p. 122—125°, which is condensed with $\text{CHMeBr} \cdot \text{CO}_2\text{Et}$ and Zn turnings in boiling C_6H_6 and then dehydrated by KHSO_4 to *Et* α -methyl- Δ^u -heptadienoate (I), m.p. 94—95°/11 mm. Condensation of (I) with $\text{Et}_2\text{C}_2\text{O}_4$ and KOEt in EtOH- Et_2O affords *Et}_2* α -keto- β - Δ^u -dimethyl- Δ^u -hexadiene- α -dicarboxylate, m.p. 70°. This is con-

verted by Ac_2O at 200° into the corresponding *Ac* derivative, reduced (Al-Hg in moist Et_2O) to the compound,

$\text{CO}_2\text{Et}\cdot\text{CH}(\text{OAc})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, which is hydrolysed to $\alpha\epsilon$ -dimethyl- $\Delta^{\alpha\gamma}$ -hexatriene- $\alpha\zeta$ -dicarboxylic acid (I), m.p. 271° (Me_2 ester, m.p. 109°), which is reduced (Na-Hg) to $\alpha\epsilon$ -dimethyl- Δ^{88} -hexadiene- $\alpha\zeta$ -dicarboxylic acid (II), m.p. 109° , isomeric with Hildebrandt's acid (III) (A., 1901, ii, 180; 1936, 1231). Addition of HBr in AcOH to (II) gives a non-cryst. acid transformed by AgNO_3 in $\text{C}_5\text{H}_5\text{N}$ into $\alpha\epsilon$ -dimethyl- $\Delta^{\gamma\epsilon}$ - or $\Delta^{\alpha\gamma}$ -hexadiene- $\alpha\zeta$ -dicarboxylic acid, m.p. 147° (Hildebrandt's ψ -acid). [The conversion of Δ^{88} -hexadiene- $\alpha\zeta$ -dicarboxylic acid into $\Delta^{\alpha\gamma}$ -hexadiene- $\alpha\zeta$ -dicarboxylic acid under similar conditions shows that the reactions are accompanied by migration of the double linkings.] Hydrogenation (Pt-SiO_2 in AcOH) of (I) affords $\alpha\epsilon$ -dimethylhexane- $\alpha\zeta$ -dicarboxylic acid, b.p. 168 – $174^\circ/0.07$ mm. (*di-p-bromophenacyl* ester, m.p. 103 – 104° or m.p. 90° when rapidly cryst. from 70 – 90% EtOH), the dichloride of which is converted by Br in strong light followed by EtOH into Et_2 $\alpha\zeta$ -dibromo- $\alpha\epsilon$ -dimethylhexane- $\alpha\zeta$ -dicarboxylate, b.p. 153 – $158^\circ/0.08$ mm. This is converted by NaI in COMe_2 into the corresponding I_2 -compound, which is transformed by 35% KOH-MeOH into $\alpha\epsilon$ -dimethyl- $\Delta^{\alpha\epsilon}$ -hexadiene- $\alpha\zeta$ -dicarboxylic acid, m.p. 193° , identical with (III).

The following examples are cited of the influence of choice of materials on the synthesis of methylated polyenedicarboxylic acids by the $\text{Et}_2\text{C}_2\text{O}_4$ process. $\text{Et } \Delta^{\alpha}$ -pentenoate, b.p. 156 – 158° , $\text{Et}_2\text{C}_2\text{O}_4$, and KOEt afford Et_2 δ -keto- γ -methyl- Δ^{α} -butene- $\alpha\delta$ -dicarboxylate, m.p. 60° , converted by the successive action of Ac_2O and Al-Hg followed by hydrolysis into β -methylmuconic acid, m.p. 232° , in 36.5% yield, whereas a yield of 34.5% is secured when $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ is the initial material. $\text{Et } \Delta^{\alpha\gamma}$ -heptadienoate, b.p. 90 – $92^\circ/12$ mm., is transformed into Et_2 ζ -keto- ϵ -methyl- $\Delta^{\alpha\gamma}$ -hexadiene- $\alpha\zeta$ -dicarboxylate, whence ϵ -methyl- $\Delta^{\alpha\gamma\epsilon}$ -hexatriene- $\alpha\zeta$ -dicarboxylic acid, m.p. 245 – 246° , in 13% yield. The yield is only about 5% when the acid is obtained similarly from $\text{Et } \beta$ -methylsorbate through the non-cryst. Et_2 ζ -keto- β -methyl- $\Delta^{\alpha\gamma}$ -hexadiene- $\alpha\zeta$ -dicarboxylate.

H. W.

Glyoxal. IV. *dl*-Tartronaldehydic acid.

H. O. L. FISCHER, E. BAER, and H. NIDICKER (Helv. Chim. Acta, 1937, 20, 1226–1236).—The prep. of cryst. *dl*-tartronaldehydic acid (I) or of salts thereof of const. composition has not been accomplished, but it is shown that in aq. solutions it has the reactions expected of a OH -aldehyde, whilst in acid solution the reducing power is so marked as to resemble that of reductone or ascorbic acid. Glyceraldehyde CH_2Ph cycloacetal in AcOH is converted by conc. H_2SO_4 followed by CrO_3 into tartronaldehydic acid $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{O}\cdot\text{CH}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$, m.p. 180 – 181° , [Na_2 salt (+ H_2O); Me_2 ester, m.p. 137 – 138°], converted by reductive fission or by hydrolysis into (I). Alternatively, glyoxal semiacetal is transformed by ClCO_2Me and KCN into the Et_2 acetal of carbomethoxytartronaldehydonitrile, $(\text{OEt})_2\text{CH}\cdot\text{CH}(\text{O}\cdot\text{CO}_2\text{Me})\cdot\text{CN}$, b.p. 131 – $133^\circ/12$ mm.

(corresponding CO_2Et -compound, b.p. 85 – $88^\circ/0.01$ – 0.03 mm., 103 – $105^\circ/1$ mm.), whence the amide, m.p. 122 – 123° (corresponding carbethoxy-amide, m.p. 75°), transformed into the Et_2 acetal of *Ba* tartronaldehydate, which is converted by CO_2 into (I). Treatment of warm solutions of (I) with $\text{NHPh}\cdot\text{NH}_2$ gives CO_2 and glyoxaldiphenylhydrazone. The phenylosazone of (I), m.p. 209° when rapidly heated, has been obtained in small amount. The Et_2 acetal of *Et* carbomethoxytartronaldehydate and the corresponding carbethoxy-compound have b.p. 85 – $90^\circ/0.02$ mm. and 90 – $95^\circ/0.02$ mm., respectively.

H. W.

Sensitised photolysis of malic acid. E. BAUR (Helv. Chim. Acta, 1937, 20, 974–977).—Irradiation of malic acid and HgCl_2 in presence of UO_2SO_4 gives HgCl and CO_2 (1 : 1), whilst AcCO_2H is produced. In presence of $\text{Fe}_2(\text{SO}_4)_3$ the ratio is 1 : 2 and MeCHO arises secondarily from AcCO_2H , whilst in presence of quinine the ratio becomes approx. 1 : 3 and MeCHO is not formed solely from AcCO_2H .

H. W.

Derivatives of hydroxymethoxysuccinic acids, and some related amides. R. T. WILLIAMS (J.C.S., 1937, 1517–1518).—*meso*-Tartaric acid, methylated ($\text{Me}_2\text{SO}_4\text{-KOH}$) and esterified (MeOH-HCl) affords Me_2 *dl*-erythro- α -hydroxy- β -methoxysuccinate, b.p. 107 – 109° (bath)/ 0.5 mm., $[\alpha]_D^{20} 0^\circ$ in MeOH (diamide, m.p. 195 – 196° ; bismethylamide, m.p. 125°). Similarly, *r*-tartaric acid yields Me_2 *dl*-threo- α -hydroxy- β -methoxysuccinate, b.p. 140° (bath)/ 2 mm. (diamide, m.p. 192 – 193° ; bismethylamide, m.p. 152 – 153°). The following are also described: *dl*-tartramide, m.p. 226° , *meso*-tartramide, m.p. 189 – 190° , *dl*-dimethoxysuccindiamide, m.p. 268 – 272° (decomp.), *dl*-tartarobismethylamide, m.p. 204 – 205° , *meso*-tartarobismethylamide, m.p. 182 – 183° , *dl*-dimethoxysuccinobismethylamide, m.p. 194 – 195° .

J. D. R.

Crystallised *l*-threonolactone and synthesis of *l*-threonic acid α -methyl ether. K. GÄTZT and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 1298–1303).—Oxidation of *l*-ascorbic acid with KMnO_4 leads to cryst. *l*-threonolactone (I), m.p. 65 – 68° (corr.), b.p. 145 – $147^\circ/0.3$ mm., $[\alpha]_D^{21} +30.7^\circ$ to $+27.3^\circ$ in H_2O , $[\alpha]_D^{20} +47.0^\circ$ in MeOH , $+45.1^\circ$ in COMe_2 , readily transformed into *l*-threonphenylhydrazide, m.p. 161 – 161.5° (corr.), $[\alpha]_D^{20} +30.9^\circ$ in H_2O , $[\alpha]_D^{21} +48.6^\circ$ in MeOH . $\text{NH}_3\text{-MeOH}$ and (I) at room temp. afford *l*-threonamide, m.p. 105.5 – 107° (corr.), $[\alpha]_D^{21} +56.0^\circ$ in H_2O , $[\alpha]_D^{20} +82.1^\circ$ in MeOH . Brucine and (I) in $\text{H}_2\text{O-MeOH}$ afford brucine *l*-threonate, m.p. 209 – 210° (corr.), $[\alpha]_D^{22} -19.3^\circ$ in H_2O ; the corresponding quinine and strychnine salts have m.p. 169.5 – 170.5° (corr.), $[\alpha]_D^{22} -116.7^\circ$ in H_2O , and m.p. 182 – 184° (corr.), $[\alpha]_D^{21} -18.5^\circ$ in H_2O , respectively. Treatment of (I) in dioxan with a large excess of CH_2N_2 in Et_2O gives *l*-threonolactone *Me* ether, m.p. 111 – $114^\circ/0.12$ mm., $[\alpha]_D^{20} +78.8^\circ$ in MeOH , characterised as *l*-threonamide α -*Me* ether, m.p. 105.5 – 107° , identical with that derived from isopropylideneascorbic acid, the structure of which is thereby elucidated.

H. W.

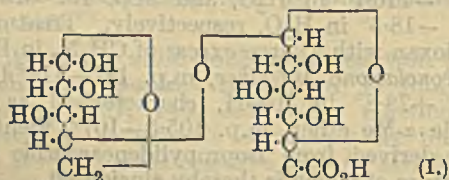
Reductones. F. MICHEEL, G. BODE, and R. SIEBERT (Ber., 1937, 70, [B], 1862–1866).—Tetronic

acid is converted by PhN_2Cl into the sparingly sol. monophenylhydrazone of hydroxydehydrotetrone acid, which with $\text{NHPh}\cdot\text{NH}_2$ gives the corresponding diphenylhydrazone. This is suspended in abs. EtOH and hydrogenated (Pd sponge) to 3:4-diaminotetrone (I), $\begin{array}{c} \text{C}(\text{NH}_2)-\text{CO} \\ | \\ \text{C}(\text{NH}_2)-\text{CH}_2 \end{array} > \text{O}$, m.p. 198—201° (decomp). Dehydro-*l*-ascorbic acid diphenylhydrazone is similarly transformed into hydroxy-3:4-diamino-5-*l*-tetronyl-acetic acid (II), $\begin{array}{c} \text{C}(\text{NH}_2)-\text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H} \\ | \\ \text{C}(\text{NH}_2)-\text{CO} \end{array}$. In H_2O (I) and (II) are nearly neutral to indicators. In acid solution AgNO_3 is reduced to Ag and 2 I are absorbed, but the changes do not occur so readily as with ascorbic or scorbaric acid. The absorption spectra of (I) and (II) suggest the presence of the forms $\begin{array}{c} \text{C}(\text{NH})-\text{CO} \\ | \\ \text{CH}(\text{NH}_2)-\text{CH}_2 \end{array} > \text{O}$ and $\begin{array}{c} \text{C}(\text{NH}) \cdot \text{CO} \cdot \text{O} \\ | \\ \text{CH}(\text{NH}_2)-\text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H} \end{array}$ in neutral solution. H. W.

Duality of the reversibly oxidised forms of vitamin-C and the polarisation of its dienol group. N. BEZSSONOFF and M. WOŁOSZYN (Nature, 1937, 139, 469).—The reversible behaviour of the blue and green solutions obtained by treating acid solutions of vitamin-C (I) with phosphomolybdic acid (II) affords further evidence of the existence of two reversibly oxidised forms of (I). Quinol (III), but not pyrocatechol, gives the same colour reactions with (II) as does (I), which indicates that in both (I) and (III) the dienol group is polarised. L. S. T.

$\beta\epsilon$ -Anhydromannono- γ -lactone. F. VALENTIN (Coll. Czech. Chem. Comm., 1937, 9, 315—326).—3:6-Anhydromannose treated with Br in H_2O for several days gives non-cryst. $\beta\epsilon$ -anhydromannonic acid (I) (amorphous Ba salt), which yields a phenylhydrazide, m.p. 190.5° (decomp.), $[\alpha]_D^{25} +19.7^\circ$ in MeOH. This with $\text{EtOH}-\text{H}_2\text{O}-\text{PhCHO}$ at the b.p. gives the γ -lactone, m.p. 113°, $[\alpha]_D^{25} +126.5^\circ$ in H_2O , falling slowly to $+115.3^\circ$ after 282 hr. K₂ saccharate reacts violently with $\text{AcCl}-\text{H}_2\text{SO}_4$, giving $\alpha\delta$ -diacetylsaccharo- $\gamma\gamma'$ -dilactone, m.p. 190—192°, $[\alpha]_D^{25} +155^\circ$ in Ac_2O . It is concluded that the two rings of these and of other sugar compounds containing the dicyclic system $\begin{array}{c} \text{O} \cdot \text{C} \cdot \text{C} \\ | \quad | \\ \text{C} \cdot \text{C} \cdot \text{O} \end{array} > \text{C}$ have the same optical character, $[\alpha]$ thus being augmented, and that the effect increases with the no. of CO groups. E. W. W.

Polysaccharides. X. Constitution of new disaccharide "xyloglucuronic acid" from *Kadsura japonica*, Don. K. NISHIDA and H. HASHIMA (Bull. Agric. Chem. Soc. Japan, 1937, 13, 660—672; cf. A., 1935, 964).—Xyloglucuronic acid (I) on methyl-

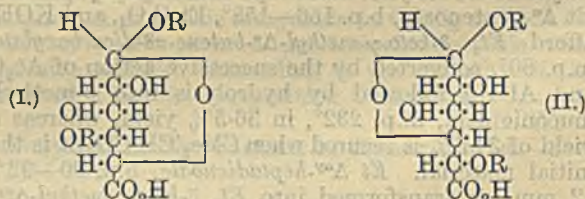


ation with $\text{Me}_2\text{SO}_4 + \text{NaOH}$ and $\text{MeI} + \text{Ag}_2\text{O}$ yielded *Me* hexamethylallobionate, $[\alpha]_D^{25} +90.7^\circ$, which on

hydrolysis with 2% HCl gave 2:3-dimethylxylose and $\alpha\beta$ -trimethylglucuronic acid. J. N. A.

Derivatives of *d*-galacturonic acid. III. Synthesis of a mercaptal of *d*-galacturonic acid and methyl tetra-acetylaldehyde-*d*-galacturonate. H. A. CAMPBELL and K. P. LINK (J. Biol. Chem., 1937, 120, 471—479).—The reaction product of *d*-galacturonic acid and EtSH in conc. HCl gives, with NaOH-MeOH, the Na salt (I), $[\alpha]_{589.3}^{25} -13.6^\circ$ in H_2O , of digalacturonic acid *Et*₂ mercaptal (II), m.p. 132.5°, $[\alpha]_{589.3}^{25} +17^\circ$ in MeOH. An aq. solution of (II) evaporated at 100° gives *d*-galacturonolactone *Et*₂ mercaptal, m.p. 79°, $[\alpha]_{589.3}^{25} +36^\circ$ in H_2O . CH_2N_2 and (II), or MeOH-HCl and (I) or (II), or Me *d*-galacturonate and EtSH in HCl, give the *Me* ester (III), m.p. 133—134°, $[\alpha]_{589.3}^{25} +17.8^\circ$ in 95% EtOH, of (II). Acetylation of (III) ($\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$) yields *Me* tetra-acetyl-*d*-galacturonate *Et*₂ mercaptal, m.p. 112.5—113.5°, $[\alpha]_{589.3}^{25} +20.5^\circ$ in CHCl_3 . This is converted ($\text{CdCO}_3-\text{HgCl}_2-\text{COMe}_2-\text{H}_2\text{O}$) into the *Et* hemiacetal (IV), sintering at 113°, m.p. 139°, $[\alpha]_{589.3}^{25} +16.5^\circ$ after 10 min., -3.0° after 36 hr., in $\text{C}_2\text{H}_2\text{Cl}_4$, of *Me* tetra-acetylaldehyde-*d*-galacturonate, m.p. 136.5—137.5°, $[\alpha]_{589.3}^{25} -16.2^\circ$ in $\text{C}_2\text{H}_2\text{Cl}_4$, of which the semicarbazone, m.p. 219—220° (decomp.), $[\alpha]_{589.3}^{25} +83.4^\circ$ in CHCl_3 , is obtained from (IV). E. W. W.

Oxidation and hydrolysis of polygalacturonide methyl ester to *l*-tartaric acid. P. A. LEVENE and L. C. KREIDER (J. Biol. Chem., 1937, 120, 591—595).—Polygalacturonide Me ester (A., 1934, 633;

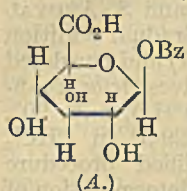


1935, 732) is oxidised (H_5IO_6 ; SrCO_3 ; Br; H_2SO_4 ; Ag_2CO_3 ; H_2S) and hydrolysed to K H *l*-tartrate, and must therefore have structure (I) or (II) (R = galacturonide residue). E. W. W.

Ring structure of α -methyl-*d*-galacturonide and its derivatives. P. A. LEVENE and L. C. KREIDER (J. Biol. Chem., 1937, 120, 597—606).—The pyran structure of methylgalacturonide (A., 1934, 281) is confirmed. α -Methyl-*d*-galacturonide Me ester monohydrate (I) (A., 1934, 280) is dehydrated in vac. at 78° over P_2O_5 to the anhyd. form, m.p. 148°, which with $\text{MeI}-\text{Ag}_2\text{O}-\text{MeOH}$ (repeated methylation) yields α -methyl-2:3:4-trimethyl-*d*-galacturonide *Me* ester, m.p. 70.2—70.3°, $[\alpha]_D^{25} +142.1^\circ$ in CHCl_3 . This is oxidised (HNO_3 , *d* 1.42, at 65—95°) to $\beta\gamma\delta$ -trimethoxymucic acid, m.p. 100—101°, $[\alpha]_D^{25} +42.0^\circ$ in COMe_2 [*Me*₂ ester, m.p. 100.5° (mixed m.p. with acid, 79—82°), $[\alpha]_D^{25} +28.9^\circ$ in H_2O ; di(methylamide), m.p. 207°, $[\alpha]_D^{25} +12.6^\circ$ in MeOH], with a syrup from which MeOH-HCl gives trimethoxy-*l*-araboglutaridi(methylamide) (A., 1927, 1059). With NH_3-MeOH , (I) gives α -methyl-*d*-galacturonamide (II), m.p. 225—226°, $[\alpha]_D^{25} +127.2^\circ$ in H_2O . After attempted "Weerman degradation" (A., 1917, i, 546) of (II), only (II) is isolated. Attempted Hofmann degradation

gives only α -methyl-*d*-galacturonide dihydrate (A., 1934, 280). E. W. W.

Chemical constitution of benzoylglucuronic acid. W. F. GOEBEL (Science, 1937, 86, 105—106).—Benzoylglucuronic acid (I) in MeOH with CH_2N_2 at -10° yields the *Me* ester, m.p. 190—191°, $[\alpha]_D^{25} -16.3^\circ$ in MeOH, acetylated ($\text{C}_5\text{H}_5\text{N}-\text{Ac}_2\text{O}$ at 0°) to *Me triacetylmonobenzoylglucuronate*, m.p. 145°, $[\alpha]_D^{25} -16.6^\circ$ in CHCl_3 . Synthetic



$\text{Me } \alpha$ -benzoyl- $\beta\gamma\delta$ -triacetylglucuronate, from *Me* α -bromo- $\beta\gamma\delta$ -triacetylglucuronate (II) and AgOBz in CHCl_3 , is identical with the corresponding derivative prepared from natural (I). It is regarded as having the same structure and configuration as (II), which is a pyranose derivative with the β configuration (A., 1936, 1231). (I) is as (A) in which Bz is attached to the first C. L. S. T.

Reactions of the thiol group. IV. N. HELLSTRÖM (Svensk Kem. Tidskr., 1937, 49, 201—207).— $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ (I) and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ after 17 days at room temp. are treated with CuSO_4 to give *Cu* α -(β -hydroxyethyl)thiolacetate, decomp. 171° . By similar methods (I) yields with $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ (II), *Cu* α -($\beta\gamma$ -dihydroxypropyl)thiolacetate, (III), decomp. 182° . (III) is also made from (I) and glycidol. (II) and carbonyl sulphate give a compound, $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$, b.p. 146° , probably α -chloro- $\beta\gamma$ -methylenedioxypropane, which with (I) yields (III). (I) and epichlorohydrin give *Cu* α -(γ -chloro- β -hydroxypropyl)thiolacetate, decomp. 157 — 158° , and *Cu* $\alpha\gamma$ -(β -hydroxypropyl)dithioldiacetate, decomp. 149° . M. H. M. A.

Mechanism of homogeneous thermal decomposition of gaseous acetaldehyde.—See A., I, 523.

Influence of traces of oxygen on thermal decomposition of gaseous acetaldehyde.—See A., I, 571.

Electrolytic reduction of *n*-valeraldehyde to *n*-pentane. S. SWANN, jun., and E. W. FIELD (Trans. Electrochem. Soc., 1937, 72, Preprint 16, 229—233).—Highest yields are obtained under conditions similar to those used for reduction of COMePr^a (A., 1935, 310) using a Cd cathode, although the yield of C_5H_{12} is much less from Bu^aCHO . The next best yield is given by $>99.99\%$ Pb, but this is very sensitive to impurities. A Zn cathode also gives a good yield. A 99.9% Pb cathode "prepared" according to Tafel (A., 1900, ii, 588) is not as efficient as pure Pb. F. R. G.

Polyene pigment of the orange. II. Citraurin. L. ZECHMEISTER and P. TUZSON (Ber., 1937, 70, [B], 1966—1969; cf. A., 1936, 1435).—The finely powdered, dried skins are extracted with Et_2O free from peroxides. The extract is evaporated, the residue is dissolved in light petroleum and chromatographed (CaCO_3). The ester fraction is hydrolysed and the hydrolysate is again chromatographed, thereby yielding citraurin (I), $\text{C}_{20}\text{H}_{40}\text{O}_2$, m.p. 146 — 147° (oxime). A method of determining (I) is given. H. W.

R* (A., II.)

Ketones from higher fatty acids. II. Comparison of the degrees of decomposition of the carboxyl group during the action of iron or magnesium powder on higher fatty acids at high temperatures. K. KINO (J. Soc. Chem. Ind. Japan, 1937, 40, 235—236B).—Decomp. is more rapid when higher temp. and large amounts of metal are used, and is greater with Fe, which also gives a more highly coloured product than Mg. Prolonged heating lowers the m.p. of the product, especially with Fe. F. R. G.

Determination of acetoin. Y. TOMIYASU (J. Agric. Chem. Soc. Japan, 1937, 13, 787—790).—Acetoin (I) in neutral or slightly acid solution is mixed with FeCl_3 and distilled into a solution containing NH_2OH , NaOAc , and NiCl_2 ; wt. of ppt. $\times 0.72 =$ (I). With a mixture of Ac_2 and (I), two determinations are necessary, the first without FeCl_3 . Wt. of ppt. $\times 0.596 = \text{Ac}_2$. J. N. A.

Syntheses of simpler methylated sugars. H. O. L. FISCHER, E. BAER, H. POLLOCK, and H. NIDECER (Helv. Chim. Acta, 1937, 20, 1213—1226).—The action of $0.1\text{N}-\text{H}_2\text{SO}_4$ on $\text{CH}_2\text{O} > \text{C}:\text{CH}_2$ gives equiv. amounts of CH_2O and acetal which condense after addition of a small excess of $\text{Ba}(\text{OH})_2$ to butane- $\alpha\beta$ -diol- γ -one (I), b.p. 65 — $70^\circ/0.02$ mm., m.p. 37.5° , also obtained by hydrolysis of isopropylidenebutane- $\alpha\beta$ -diol- γ -one or by oxidation of $\text{COMe}\cdot\text{CH}:\text{CH}_2$ with NaClO_3 in presence of OsO_4 or, less advantageously, of KMnO_4 . (I) affords a hydrazone, m.p. 110 — 111° , 2:4-dinitrophenylhydrazone, m.p. 118° , 2:4-dinitrophenyllosazone, a diacetate, b.p. 51 — $64^\circ/0.01$ — 0.02 mm., and its *p*-nitrophenylhydrazone, m.p. 105° , a dibenzoate, m.p. 87° , and a methylcycloacetal (bimol.), m.p. 177 — 178° . Distillation with P_2O_5 transforms (I) into Ac_2 . Condensation of (I) with CH_2O or of $\text{COMe}\cdot\text{CH}_2\cdot\text{OH}$ with CH_2O (1:2) affords γ -hydroxymethylbutane- $\gamma\delta$ -diol- β -one (dihydroxymethylacetol), b.p. 105 — $107^\circ/0.02$ — 0.05 mm. (2:4-dinitrophenylhydrazone, m.p. 156 — 157° ; tri-*p*-nitrobenzoate, m.p. 192 — 194° ; anhydride $\text{C}_{10}\text{H}_{16}\text{O}_6$, m.p. 196 — 197° , and its diacetate, m.p. 196°).

Oxidation of mesityl oxide in COMe_2 by NaClO_3 and a little OsO_4 in H_2O and treatment of the mixture with Zn powder yields β -methylpentane- $\beta\gamma$ -diol- δ -one (trimethylglycerose), b.p. 94 — $99^\circ/9$ mm., m.p. 20 — 21° (2:4-dinitrophenylhydrazone, m.p. 157 — 158° ; di-*p*-nitrobenzoate, m.p. 154 — 155°). H. W.

Dioximes. CXXII. G. TAPPI (Gazzetta, 1937, 67, 388—392).—Dimethyltriketone trioxime (I) with N_2O_4 gives methylacetylglaxyoxime peroxide oxime, $\text{CMe}-\text{C}(\text{Me})\cdot\text{N}\cdot\text{OH}$ (II), m.p. 130 — 131° (*Ac*, m.p. 73° , and *Bz*, m.p. 172° , derivatives), which in HNO_3 (*d* 1.40) gives dinitromethylacetylglaxyoxime peroxide, m.p. 72 — 73° , converted by $\text{SnCl}_2\cdot\text{HCl}$ into methylacetylglaxyoxime peroxide. Hydrolysis of (II) by 20% HCl gives methylacetylglaxyoxime peroxide, m.p. 32 — 33° (phenylhydrazone, m.p. 169° ; semicarbazone, m.p. 230°). Using excess of N_2O_4 , (I) also yields traces of dimethyltriketone-1:3-dioxime peroxide 2-oxime, m.p. 182° (decomp.), converted by $\text{NH}_2\text{OH}\cdot\text{HCl}$ in $\text{C}_5\text{H}_5\text{N}$ into (I). E. W. W.

Oxidation as a route to carbohydrates. N. A. ORLOV and L. S. MUSTAFIN (Compt. rend. Acad. Sci. U.R.S.S., 1937, 16, 107—108).—Dipentene, allyl alcohol, and styrene in H_2O with $\text{Ca}(\text{OH})_2$, active C, and O_2 at 100—110° in 34 days afford pentosans (0.03—0.1% yield). J. D. R.

Sugars in solution and in the cell. E. F. ARMSTRONG (Chem. & Ind., 1937, 816—818).—The tautomerism of sugars in solution and the probable modes of biogenesis of sugars are discussed.

R. S. C.

2 : 5-Dimethylxylofuranose and 2 : 3-dimethylxylose. G. J. ROBERTSON and D. GALL (J.C.S., 1937, 1600—1604).—1 : 2-*iso*Propyridenexylose 5-benzoate 3-*p*-toluenesulphonate is hydrolysed (NaOMe in C_6H_6) to 1 : 2-*isopropylidenexylose* 3-*p*-toluenesulphonate, m.p. 89—90°, $[\alpha]_D^{25}$ —28.6° in CHCl_3 , which with MeI- Ag_2O yields 5-methyl-1 : 2-*isopropylidenexylose* 3-*p*-toluenesulphonate, m.p. 81—82°, $[\alpha]_D^{18}$ —31.8 in CHCl_3 , converted by MeOH-HCl into 5-methyl- β - (I), m.p. 89°, $[\alpha]_D^{18}$ —51.7° in CHCl_3 , and - α -methylxylofuranoside 3-*p*-toluenesulphonate (II) (a syrup), $[\alpha]_D^{18}$ +44.5° in CHCl_3 ; the α - and β -forms are converted by HCl-MeOH into an equilibrium mixture, $[\alpha]_D$ +11.7° in CHCl_3 . Methylation of (I) and (II) (MeI- Ag_2O) affords respectively 2 : 5-dimethyl- β - (a syrup), $[\alpha]_D^{18}$ —49.9°, and - α -methylxylofuranoside 3-*p*-toluenesulphonate (a syrup), $[\alpha]_D^{17}$ +34.7° in CHCl_3 , which are hydrolysed (KOH-aq. EtOH) to 2 : 5-dimethyl- β -, b.p. 85°/0.02 mm., $[\alpha]_D^{17}$ —56° in CHCl_3 , and - α -methylxylofuranoside, b.p. 110°/0.03 mm., $[\alpha]_D^{17}$ +54.3° in CHCl_3 , both of which are converted (HCl-aq. COMe_2) into 2 : 5-dimethylxylofuranose (a syrup), $[\alpha]_D^{17}$ +46° in H_2O , +16.4° in EtOH. This, with *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$ yields the *p*-bromophenylosazone of 5-methylxylose. 1 : 2-*iso*Propyridenexylose 5-benzoate, hydrolysed (MeOH-HCl) and methylated (Ag_2O -MeI), gives 2 : 3-dimethyl- γ -methylxyloside 5-benzoate (a syrup), hydrolysed (NaOH-aq. EtOH) to 2 : 3-dimethyl- γ -methylxyloside, b.p. 95°/0.15 mm., $[\alpha]_D^{18}$ +12.5° in CHCl_3 , and further hydrolysed (aq. HCl) to 2 : 3-dimethylxylose, identical with that obtained from xylan by Robertson and Speedie (A., 1934, 871). 1 : 2-*iso*Propyridenexylose 5-*p*-toluenesulphonate when methylated (MeI- Ag_2O) yields 3-methyl-1 : 2-*isopropylidenexylose* 5-*p*-toluenesulphonate, m.p. 114°, $[\alpha]_D$ —27.2° in CHCl_3 , hydrolysed (HCl-MeOH) to monomethylmethylxyloside.

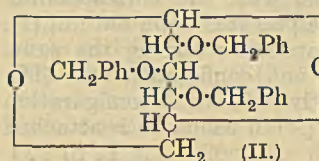
J. D. R.

β -D-Talose and d-talose acetates and orthoesters. W. W. PIGMAN and H. S. ISBELL (J. Res. Nat. Bur. Stand., 1937, 19, 189—213).—Oxidation (BzO_2H) of galactal by Levene and Tipson's method (A., 1931, 938) affords galactose, α - (I) and β -d-talose (II), m.p. 120—121°, and d-talose benzoate (III), m.p. 150—170° (decomp.). Acetylation ($\text{C}_5\text{H}_5\text{N}\cdot\text{Ac}_2\text{O}$; 0°; 3 days) of (I) yields α -d-talose pentaacetate, m.p. 106.5—107°, $[\alpha]_D^{20}$ +70.2° in CHCl_3 , which with AcOH containing 38% of HBr (0°, 1 hr. followed by room temp., 2½ hr.) affords 1-bromo-d-talose tetraacetate (IV), m.p. 84—84.5° (sinters 83°), $[\alpha]_D^{20}$ +165.6° in CHCl_3 . (IV) with $\text{AcOH}\cdot\text{Ag}_2\text{CO}_3$ (0°, 1½ hr.) gives d-talose triacetate 1 : 2-*o*-methylacetate, m.p. 91.5—92.5°, $[\alpha]_D^{20}$ +3.7° \rightarrow +2.2°

(19 hr.), and with AgOBz in moist COMe_2 (—4°; 1½ hr.) yields α -d-talose tetraacetate, m.p. 112—113°, $[\alpha]_D^{20}$ +42.8° in CHCl_3 . Mutarotation and oxidation ($\text{Br}\cdot\text{H}_2\text{O}$) rates are given for (I) and (II), and evidence is given suggesting that (III) has an orthobenzoic acid structure. The conditions for ortho-ester formation are discussed.

F. N. W.

Benzylated derivatives of β -glucosan and of glucose. G. ZEMPLÉN, Z. CSÜRÖS, and S. ANGYAL (Ber., 1937, 70, [B], 1848—1856).—Gradual addition of a mixture of β -glucosan triacetate (I) and powdered KOH to CH_2PhCl at 95—100° gives tribenzyl- β -glucosan (II), m.p. 90°, $[\alpha]_D^{25}$ —29.5° in CHCl_3 (a modified procedure for the determination of CH_2Ph is recorded). (II) with Ac_2O containing a trace of conc. H_2SO_4 at room temp. gives α -



2 : 3 : 4-tribenzylglucose 1 : 6-diacetate, m.p. 66°, $[\alpha]_D^{21}$ +62.5° in CHCl_3 , $[\alpha]_D^{20}$ +81.5° in EtOH, and the corresponding β -derivative. The mixture is hydrolysed by NaOMe-MeOH at room temp. to a mixture of α - and β -tribenzylglucose, giving after treatment with Ac_2O and anhyd. NaOAc at 100° a product from which β -2 : 3 : 4-tribenzylglucose 1 : 6-diacetate, m.p. 63—63.5°, $[\alpha]_D^{21}$ +17.4° in CHCl_3 , is isolated. This, or its mixture with the α -isomeride, in CHCl_3 is transformed by HBr-AcOH followed by $\text{CH}_2\text{Ph}\cdot\text{OH}$ and Ag_2CO_3 in C_6H_6 into 2 : 3 : 4-tribenzyl- β -benzylglucoside 6-acetate, m.p. 115.5—116°, $[\alpha]_D^{21}$ +2.9° in CHCl_3 , which with CH_2PhCl and KOH at 95—100° affords 1 : 2 : 3 : 4 : 6-pentabenzylglucose, m.p. 82—82.5°. 2 : 4-Dibenzyl- β -glucosan (III), m.p. 103°, $[\alpha]_D^{20}$ —28.5° in CHCl_3 , is invariably produced during the prep. of (II) and is conveniently obtained when solid KOH is added to a mixture of (I) and CH_2PhCl in xylene at 90°; it passes into 2 : 4-dibenzylglucose, m.p. 75—79°, $[\alpha]_D^{18}$ +25.1° in EtOH. The constitution of (III) is established by converting it into 2 : 4-dibenzyl- β -glucosan-3-*p*-toluenesulphonate, m.p. 105.5—106°, $[\alpha]_D^{17}$ —5.7° in CHCl_3 ; this is debenzylated by hydrogenation (Pd-C in EtOH-AcOH) and the product is transformed by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at room temp. into β -glucosan 2 : 4-diacetate 3-*p*-toluenesulphonate (IV), m.p. 87—87.5°. Treatment of (IV) with $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$ followed by HBr-AcOH affords α -bromoglucose 2 : 4 : 6-triacetate 3-*p*-toluenesulphonate, m.p. 150°, which with Ac_2O and TiOAc yields β -glucose 1 : 2 : 4 : 6-tetraacetate 3-*p*-toluenesulphonate, m.p. 171—172°.

H. W.

Aldehydo-derivatives of dibenzylideneglucose. M. L. WOLFROM and L. J. TANGHE (J. Amer. Chem. Soc., 1937, 59, 1597—1602).—When glucose Et_2 mercaptal 6-benzoate (I), PhCHO , and ZnCl_2 react, $[\alpha]$ rapidly passes through a min. and then rises. This min. α corresponds with a max. yield of dibenzylidene-d-glucose *Et*₂ mercaptal 6-benzoate (II), m.p. 130.5—131.5°, $[\alpha]_D^{23}$ —15.5° in CHCl_3 , —11° in PhCHO [hydrolysed to (I) by hot aq. AcOH], which passes by further reaction into dibenzyliden-d-glucose 6-benzoate (III), m.p. 160—160.5°, $[\alpha]_D^{25}$ +15° in CHCl_3 , $[\alpha]_D^{25}$ +18° in $\text{C}_2\text{H}_2\text{Cl}_4$, +20° in

PhCHO (does not reduce Fehling's solution or AgNO_3). $\text{CdCO}_3\text{-HgCl}_2$ in aq. COMe_2 converts (I) into *di-benzylidene-aldehyde-d-glucose 6-benzoate*, m.p. 185—187°, non-reducing, $[\alpha]_D^{20} +43^\circ$ (stable) in $\text{C}_2\text{H}_5\text{Cl}_4$, $[\alpha]_D^{25} +51^\circ \rightarrow +14^\circ$ (24 hr.) in CHCl_3 containing EtOH [thiosemicarbazone, m.p. 191—192° (decomp.), $[\alpha]_D^{25} +47^\circ \rightarrow +40^\circ$ in CHCl_3], which gives Schiff's test and is converted by PhCHO- ZnCl_2 into (II). Hot 0.5N-NaOH hydrolyses (II) to 2:3:4:5-*dibenzylidene-d-glucose Et_2 mercaptal*, m.p. 159.5—160.5°, $[\alpha]_D^{25} -17^\circ$ in CHCl_3 , reconverted into (II) by benzoylation and giving with $\text{HgCl}_2\text{-CdCO}_3$ 2:3:4:5-*dibenzylidene-d-glucose*, amorphous [thiosemicarbazone, m.p. 223—224° (decomp.), $[\alpha]_D^{25} +91^\circ$ in $\text{C}_5\text{H}_5\text{N}$]. Hydrolysis of (III) gives *dibenzylidene-d-glucose*, m.p. 163—165°, $[\alpha]_D^{25} +35^\circ$ in $\text{C}_5\text{H}_5\text{N}$, reconverted into (III) by benzoylation. R. S. C.

Acetylation and methylation of agar-agar and the isolation of 2:4:6-trimethyl- α -D-galactose by hydrolysis. E. G. V. PERCIVAL and J. C. SOMERVILLE (J.C.S., 1937, 1615—1619).—Agar acetate with $\text{Me}_2\text{SO}_4\text{-NaOH}$ yields a product, $[\alpha]_D^{25} -92^\circ$ in CHCl_3 , which is hydrolysed (H_2SO_4 followed by MeOH-HCl) to Me lævulate (p-nitrophenylhydrazone, m.p. 136°), an unidentified dimethylmethylketoside, and 2:4:6-trimethylmethylgalactoside monohydrate (I), m.p. 37°, $[\alpha]_D^{25} +101^\circ$ in H_2O , further hydrolysed (HCl) to 2:4:6-trimethyl- α -galactose (II), m.p. 104—105°, $[\alpha]_D^{25} +124^\circ$ in H_2O , which with NHPh-NH_2 yields 4:6-dimethylgalactosazone, m.p. 158°, $[\alpha]_D^{25} -25^\circ$ in EtOH. When treated with Br and dehydrated, (I) gives 2:4:6-trimethyl- δ -galactonolactone, $[\alpha]_D^{25} +50^\circ$ in H_2O (amide, m.p. 167°, $[\alpha]_D^{25} +74^\circ$ in H_2O). With HCl-MeOH , (II) regenerates (I).

J. D. R.

Reduction of potassium dichromate by sucrose.—See A., I, 577.

Influence of the walls of the vessel on the course of alcoholic reactions. E. BERNER and A. HJULSTAD (Ber., 1937, 70, [B], 2028—2031).—Alcoholysis of heptamethyl- β -methyl-lactoside occurs almost twice as quickly in a steel tube (construction described) as in a glass tube. Similar observations are recorded for β -phenolglucoside and MeOH at 205—210° and for the action of MeOH on $\text{CH}_2\text{Ph-OAc}$ at about 210°.

H. W.

Emulsin. XXXI. Mono- and di- β -D-glucosides of dihydric alcohols and their hydrolysis by sweet almond emulsin. B. HELFERICH and R. HILTMANN (Annalen, 1937, 531, 160—175).—The ease of hydrolysis of monoglucosides $\text{OH}[\text{CH}_2]_n\text{OR}$ increases somewhat with increase in the length of the C chain. Diglucosides $\text{OR}[\text{CH}_2]_n\text{OR}$ are hydrolysed at about the same rate as the corresponding monoglucosides if $n = 2$ or 3, but much more slowly when $n = 4$. $\text{OH}[\text{CH}_2]_2\text{OMe}$, acetobromoglucose (I), and Ag_2CO_3 give β - β' -methoxyethyl-d-glucoside tetra-acetate, m.p. 81—82°, $[\alpha]_D^{20} -20.6^\circ$ in CHCl_3 , hydrolysed (Zemplén) to β - β' -methoxyethyl-d-glucoside, m.p. 117.5—119° (corr.), $[\alpha]_D^{22} -28.7^\circ$ in H_2O . β' -Hydroxyethyl- β -D-glucoside tetra-acetate, (I), Ag_2CO_3 , CaCl_2 , and I in anhyd. CHCl_3 yield glycoldi- β -D-glucoside octa-acetate, m.p. 170.5—171°, $[\alpha]_D^{20} -31.8^\circ$ in CHCl_3 , whence glycoldi- β -D-glucoside,

m.p. 113—115°, $[\alpha]_D^{20} -35.2^\circ$ in H_2O . (I) and $\text{CH}_2(\text{CH}_2\text{OH})_2$ with Ag_2CO_3 give γ' -hydroxypropyl- β -D-glucoside tetra-acetate (II), m.p. 97.5—98.5° (corr.), $[\alpha]_D^{20} -17.0^\circ$ in CHCl_3 , de-acetylated to γ' -hydroxypropyl- β -D-glucoside, m.p. 100—101.5° (corr.), $[\alpha]_D^{20} -36.2^\circ$ in H_2O . (II) and (I) in anhyd. CHCl_3 containing Ag_2CO_3 , CaCl_2 , and I give propane- $\alpha'\gamma'$ -dioldi- β -D-glucoside octa-acetate, m.p. 175—176.5° (corr.), $[\alpha]_D^{20} -16.9^\circ$ in CHCl_3 , whence propane- $\alpha'\gamma'$ -dioldi- β -D-glucoside, m.p. 152—154° (corr.) after softening, $[\alpha]_D^{20} -40.5^\circ$ in H_2O . Analogous methods are used in the prep. of the following: δ' -hydroxybutyl- β -D-glucoside, m.p. 98—100° (corr.), $[\alpha]_D^{20} -35^\circ$ [tetra-acetate, m.p. 78—80° (corr.), $[\alpha]_D^{20} -19.2^\circ$ in CHCl_3], and butane- $\alpha\delta$ -dioldi- β -D-glucoside, m.p. 184—185° after softening, $[\alpha]_D^{21} -41.9^\circ$ in H_2O , n-pentane- $\alpha'\epsilon'$ -dioldi- β -D-glucoside, m.p. 90—92° (corr.) after softening at about 80°, decomp. 100°, $[\alpha]_D^{23} -40.0^\circ$ in H_2O (octa-acetate, m.p. 122.5—124°, or, occasionally, m.p. 134.5—137°, $[\alpha]_D^{20} -24.5^\circ$ in CHCl_3); n-hexane- $\alpha'\zeta'$ -dioldi- β -D-glucoside (+ H_2O), m.p. (anhyd.) 152.5—153.5° (corr.), $[\alpha]_D^{23} -40.1^\circ$ in H_2O [octa-acetate, m.p. 142—143.5° (corr.), $[\alpha]_D^{20} -24.6^\circ$ in CHCl_3]; 1-trans-cyclopentane-1:2-diol- β -D-glucoside, $[\alpha]_D^{25} -28.5^\circ$ in H_2O ; cis-cyclopentane-1:2-diol- β -D-glucoside, two diastereoisomeric forms-I, m.p. 165—167.5° (corr.), $[\alpha]_D^{25} -24.0^\circ$ in H_2O and -II, m.p. 135.5—137.5°, $[\alpha]_D^{25} -36.3^\circ$ in H_2O ; n-butane- $\alpha'\delta'$ -diol- α' - β -D-glucoside- δ' - β -D-6-methanesulphonylglucoside, m.p. 122.5—124°, $[\alpha]_D^{23} -38.0^\circ$ in H_2O [hepta-acetate, m.p. 142—143° (corr.), $[\alpha]_D^{23} -20.4^\circ$ in CHCl_3].

H. W.

Constitution of the glucoside butrin isolated from Butea frondosa flowers. I. J. B. LAL (J.C.S., 1937, 1562—1564).—Butrin (I), $[\alpha]_D^{30} -81.7^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (dihydrate, $[\alpha]_D^{31.5} -73.27^\circ$ in H_2O), with $\text{Pb}(\text{OAc})_2$ yields a Pb salt, $\text{C}_{27}\text{H}_{30}\text{O}_3 \cdot (\text{O-Pb-OAc})_2 \cdot 2\text{H}_2\text{O}$, m.p. 128°. The following derivatives of (I) are described: nonabenzoyle (monohydrate), m.p. 141°, $[\alpha]_D^{30} +77.28^\circ$ in $\text{C}_5\text{H}_5\text{N}$, deca-acetyl (monohydrate) (by $\text{NaOAc-Ac}_2\text{O}$), m.p. 119—120°, $[\alpha]_D^{30} -79.86^\circ$ in $\text{C}_5\text{H}_5\text{N}$, oxime (dihydrate), m.p. 180°, tetra-p-nitrobenzoyl (monohydrate), m.p. 154° $[\alpha]_D^{30}$ (anhyd. material) -44.30° in $\text{C}_5\text{H}_5\text{N}$. (I) with $\text{Me}_2\text{SO}_4\text{-KOH}$ yields O-methylbutrin, m.p. 82—84°, whilst with $\text{MeI-K}_2\text{CO}_3$ in MeOH, O-dimethylbutrin (hepta-hydrate), m.p. 234°, is formed. (I) with $\text{Na}_2\text{CO}_3\text{-EtI}$ in EtOH affords O-diethylbutrin (+7.5 H_2O), m.p. 238°, and an isomeric chalkone derivative, m.p. 183°, whilst on oxidation ($\text{H}_2\text{O}_2\text{-KOH}$), fisetin is formed.

J. D. R.

Placing the oleander glycoside in the digitalis group. W. NEUMANN and W. LINDNER (Arch. exp. Path. Pharm., 1937, 185, 630—643).—The aglucone of oleandrin is identical with acetylgitoxigenin, and that of deacetyloleandrin with gitoxigenin. Both glycosides belong therefore to the digitalis group; this is borne out by the pharmacological activity.

P. W. C.

Gossypitrin. Attempt to define the position of the glucose residue. K. NEELAKANTAM and T. R. SESHADRI (Proc. Indian Acad. Sci., 1937, 6, A, 12—15).—Methylation (CH_3N_2) of gossypitrin and subsequent hydrolysis gives gossypetin (?) 3:8:3':4':

*Me*₄ ether, m.p. 227—230° after softening at 225° *Ac*₂ derivative, m.p. 142—143° after softening at 135°, methylated (*Me*₂SO₄) to the *Me*₆ ether. The glucose residue is probably in position 7. F. R. G.

Mechanism of the reduction of aromatic *N*-glucosides to arylglucamines. P. KARRER and E. HERKENRATH (Helv. Chim. Acta, 1937, 20, 1016—1019).—*N*-*p*-Toluidineglucoside tetraacetate, from acetobromoglucose and *p*-C₆H₄Me·NH₂, or by acetylation of *p*-toluidineglucoside, is reduced (Ni-H₂) as readily as the *Ac*-free compound. Under similar conditions *N*-methylanilineglucoside tetraacetate and *theophylline-d-glucoside tetraacetate* are unaffected. It appears therefore that in all cases reduction affects the Schiff's base which in solution is in equilibrium with the *N*-glucoside form.

H. W.

Rapid volumetric determination of pentosans. I. K. CHRISTITSCH (Zavod. Lab., 1937, 6, 558—561).—Furfuraldehyde (I) obtained from pentosans and boiling acid is determined by Bertrand's instead of by the usual phloroglucinol method. The Cu equiv. of (I) is almost identical with that of glucose.

R. T.

Asparagose. S. MURAKAMI (Acta Phytochim., 1937, 10, 43—62).—The tubers of *Asparagus officinalis* contain a non-reducing fructosan, *asparagose* (I), m.p. 215°, $[\alpha]_D^{20}$ —35.7°, mol. wt. 1160 (=7 fructose units) (*triacetate*, m.p. 125°, $[\alpha]_D^{20}$ —35.6° in CHCl₃, —42.6° in AcOH, mol. wt. 2211; *Me* derivative, m.p. 138—142°, $[\alpha]_D^{20}$ —50.4° in CHCl₃). (I) with NaOMe in MeOH gave a *product*, $[\alpha]_D^{20}$ —35.5°, mol. wt. 1280 (=8 fructose units). Under the same conditions, sucrose, (I), and inulin are hydrolysed by acid in 391, 558, and 840 min., the degree of hydrolysis with (I) being 87% and 94% as determined by reduction and polarimetric methods, respectively. The max. aldose val. was 1.6%. (I) in glycerol at 140° gave a *product* still having the same rotation, but the mol. wt. corresponded with that of a dihexosan. This re-associated on keeping. Similar depolymerisation occurs on heating in HCO·NH₂ and in NH₂Ac. Hydrolysis of the *Me* derivative in H₂C₂O₄-HCl gave an oil, b.p. 110—120°, $[\alpha]_D^{20}$ +26.9°, containing 41% OMe (phenylosazone, m.p. 127—128°), which resembled in properties 3:4:6-trimethylfructose.

P. W. C.

"Cremastramannan," the mannan of Japanese saleps. T. OHTSUKI (Acta Phytochim., 1937, 10, 1—28).—The tubers of *Cremastra variabilis* contain but little starch and considerable amounts of *cremastramannan* (I) $[\alpha]_D^{20}$ —46.6°±6.6° in dil. NaOH, which on acid hydrolysis gives *d*-mannose and *d*-glucose (3:1). Treatment with pancreatin and diastase gives *cremastramannin-A* (II), $[\alpha]_D^{20}$ —46.6° in 0.02*N*-NaOH, and with takadiastase *cremastramannin-B*, $[\alpha]_D^{20}$ —40° in 0.02*N*-NaOH (III), both of which on acid hydrolysis give mannose and glucose (3:1). (I), (II), and (III) all give *acetates* in which each hexose mol. has 3 OAc groups, the m.p. being 269°, 245°, and 220°, respectively; all are optically inactive in COMe₂. The dissociation by heat is followed in terms of change of viscosity. (I) gives Cu and Pb complexes, the metal contents of which

correspond with the requirements of the formulae (C₆H₁₀O₅)₈Cu, (C₆H₁₀O₅)₁₂Cu, and (C₆H₁₀O₅)₄Pb. (I) after 15 and (II) and (III) after ten treatments with *Me*₂SO₄-NaOH give sol. *derivatives* of m.p. 240°, 242°, and 247° containing >40% OMe and having $[\alpha]_D^{20}$ —36.1°~—39.7°, —37.5°, and —42.2°, respectively.

P. W. C.

Bletillamannan, a mannan from the tubers of *Bletilla striata*. T. OHTSUKI (Acta Phytochim., 1937, 10, 1—28).—The tubers contain but little starch and considerable amounts of *bletillamannan* (I), $[\alpha]_D^{20}$ —40°±5.3° in 0.5% NaOH, which on acid hydrolysis gives *d*-mannose and *d*-glucose in the ratio 4:1. Treatment with pancreatin gives *bletillamannin-A* (II), $[\alpha]_D^{20}$ —44.4° in 0.5% NaOH, and with takadiastase *bletillamannin-B* (III), $[\alpha]_D^{20}$ —44.4° in 0.5% NaOH, both of which on acid hydrolysis give mannose and glucose (4:1). (I), (II), and (III) give *acetates*, m.p. 270°, 268°, and 258°, respectively, in which each hexose mol. has 3 OAc groups, and all have $[\alpha]_D^{20}$ —32° in CHCl₃. (I), (II), and (III) on treatment 10—13 times with *Me*₂SO₄-NaOH give sol. *derivatives* of m.p. 250° containing >40% of OMe and having $[\alpha]_D^{20}$ —58°, —50°, and —40° in CHCl₃, respectively.

P. W. C.

Dextrins and the constitution of starch; phosphorus content of starch and dextrins. K. MYRBÄCK and K. AHLBORG (Svensk Kem. Tidskr., 1937, 49, 216—230).—The constitution of starch is critically reviewed with especial reference to the production of dextrins by enzymic fission. Hydrolysis of starch with β-amylase, followed by fractional pptn. of the products with EtOH, yields dextrins with *M* 8000—80,000, whilst with maltase or ptyalin, dextrins with *M* 2500—1100 are obtained. The dextrins are considered to originate from portions of the starch mol. lying between "anomaly" points, which may be chain-branching points, or points where a phosphate group occurs. Determination of the P content of native starches and of sol. starches obtained therefrom by acid hydrolysis indicates that the P-containing portion of the mol. is most resistant to hydrolysis, and similarly, determination of P in the dextrins prepared by hydrolysis with takadiastase or β-amylase shows that the P-containing portion is almost completely resistant to hydrolysis to maltose by β-amylase.

J. D. R.

Starch. IV. Hydrolysis of starch by 7.5 and 15% hydrochloric acid at low temperatures [20°]. V. Phosphoric acid content of potato-starch. A. TYCHOWSKI and S. MASIOR (Biochem. Z., 1937, 292, 141—147, 218—220; cf. A., III, 312).—IV. Results for the formation of maltose, H₂O-sol. and -insol. fractions, changes in hydrolytic products of α- and α+β-amylase action, and ash and P₂O₅ contents are tabulated and discussed.

V. Starch paste heated under pressure in presence of CaCO₃ yields the Ca salt of amylophosphoric acid (I) which is more thermostable than the original (I), decomp. only at temp. >150°. The stability is not due to *p*_H but is sp. for the Ca salt. F. O. H.

Cellulose, starch, and glycogen. H. STAUDINGER (Naturwiss., 1937, 25, 673—681).—A lecture.

Oxidation of cellulose in a heterogeneous medium. L. BRISSAUD (Mém. Poudres, 1937, 27, 195—213).—Samples of cellulose (I) were oxidised with 0.1N-NaOCl to products containing 0.069, 0.077, 0.154, 0.235, and 0.312 atoms of O per mol. of $C_6H_{10}O_5$, respectively. Reducing power and methylene-blue absorption increase rapidly with degree of oxidation. This differentiates (I) degraded by hydrolysis, which have a lower methylene-blue val. than the original (I) and relatively low reduction nos. Nitration also differentiates oxidised and hydrolysed (I); the former seem to undergo nitration like (I), but partly decompose during stabilisation. The CO_2H content increases with degree of oxidation. By treating oxidised (I) with boiling H_2O and cold 2% aq. NaOH, respectively, products having similar properties to the original (I), or rather to (I) degraded by acids, were obtained. The extracts do not appear to be impurities, that have been fixed by adsorption, but seem to form parts of chains to which they are attached by main valencies. W. J. W.

Action of sodium hypiodite on cellulose. L. BRISSAUD (Mém. Poudres, 1937, 27, 214—229).—Prolongation of the hypiodite treatment beyond $\frac{1}{2}$ hr. does not affect the amount of I consumed, but if after $\frac{1}{2}$ hr. treatment and separation of the wash waters the sample is again treated there is a further considerable consumption. This varies with the concn. of the reagents. Reducing groups are formed or appear during the treatment in addition to the development of acidity, which seems to imply the superimposing of two actions. One of these is caused by the oxidising agent and induces degradation and is analogous to the action of NaOCl. The other action causes changes on the surface of the micelles, which facilitate the passage of sol. products in the micelles. The intervention of surface effects and secondary oxidising reactions invalidates the I val. as an accurate measure of the mol. wt. of cellulose. W. J. W.

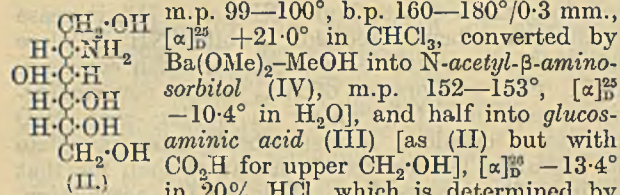
Highly polymerised compounds. CLXVIII. Determinations of the viscosity of cellulose nitrates. H. STAUDINGER and M. SORKIN (Ber., 1937, 70, [B], 1993—2017).—Cellulose nitrates (I) are obtained by the action of $HNO_3-H_2SO_4$ on cellulose of varying degree of polymerisation. They can be preserved almost unchanged over P_2O_5 if the acid has been removed completely. For sol solutions the relationship $\eta_{sp}/c_{gm.} = K_m M$ is shown to hold good by comparison of the mol. wt. determined osmotically with that based on viscosimetric measurements in $COMe_2$ or $BuOAc$. For gel solutions, the expression $\log \eta_{sp}/c_{gm.} = [\log \eta_{sp}/c_{gm.}]_{c \rightarrow 0} + c.K_{st.}$ holds for (I) and the relationship between mol. wt. and increment const. is $M = (K_{st.} + 7)/K_{mst.}$. The dependence of viscosity on temp. has been investigated. The viscosity of (I) in $BuOAc$ with increasing amounts of C_6H_6 , in $BuOAc$ + light petroleum, cyclohexane, EtOH, $CHCl_3$, CCl_4 , or $PhCl$, and in $COMe_2-H_2O$ gives results dissimilar to those observed with the polystyrenes. The low viscosity of (I) in C_5H_5N is due to degradation. The departures of solutions of (I) from the Hagen-Poiseuille law are discussed. H. W.

X-Ray diffraction study of the action of liquid ammonia on cellulose and its derivatives. G. L. CLARK and E. A. PARKER (J. Physical Chem., 1937, 41, 777—786).—Fibres of native and mercerised cellulose, treated with liquid NH_3 at -75° , increase in diameter about threefold. Swollen NH_3 -cellulose is reverted to cellulose by treatment with conc. aq. NH_3 . Slow evaporation of NH_3 yields a new modification, cellulose III, which on boiling with H_2O reverts to cellulose, reversion being more complete for cellulose III derived from native than for that derived from mercerised cellulose. On acetylation, cellulose III gives the same acetate as native and mercerised cellulose. The actions of heat, dil. and conc. NH_3 , and $AcOH$ on cellulose III have also been examined. Commercial cellulose acetates are saponified by liquid NH_3 after several days. C. R. H.

Rotatory dispersion of configuratively related amines. P. A. LEVENE, A. RUTHEN, and M. KUNA (J. Biol. Chem., 1937, 120, 759—775).—The correlation of the configuration of primary and sec. amines is similar to that of primary and sec. alcohols and the direction of rotation of the former is identical with that of the corresponding alcohols. In all alkylamines the absorption regions nearest to the visible region are not anisotropic. The following new compounds have been prepared: d- β -benzamidobutane, m.p. 86—88°, $[\alpha]_D^{25} +6.7^\circ$ in abs. EtOH; d- β -benzamidooctane, m.p. 73—74°, $[\alpha]_D^{25} +28.5^\circ$ in abs. EtOH; d-hexan- β -ol, b.p. 99—100°/168 mm., $[\alpha]_D^{25} +10.7^\circ$, converted by anhyd. HI into l- β -iodohexane, b.p. 90—91°/70 mm., $[\alpha]_D^{25} -30.7^\circ$; this with NaN_3 in $H_2O-MeOH$ at 80° gives d- β -azidohexane, b.p. 96—98°/160 mm., $[\alpha]_D^{25} +27.8^\circ$, hydrogenated (Adams) to l- β -aminohexane, b.p. 70°/155 mm., $[\alpha]_D^{25} +4.30^\circ$ (hydrochloride, $[\alpha]_D^{25} -5.68^\circ$ in abs. EtOH, transformed into d- β -benzamidohexane, m.p. 86—88°, $[\alpha]_D^{25} +14.3^\circ$ in abs. EtOH); d- γ -heptanol, b.p. 104—106°/117 mm., $[\alpha]_D^{25} +5.12^\circ$, converted successively into l- γ -iodoheptane, b.p. 76°/12 mm., $[\alpha]_D^{25} -8.25^\circ$, d- γ -azidoheptane, b.p. 79—81°/43 mm., $[\alpha]_D^{25} +1.78^\circ$, and d- γ -aminohexane, b.p. 75°/70 mm., $[\alpha]_D^{25} +4.15^\circ$ (homogeneous), $[\alpha]_D^{25} +2.6^\circ$ in abs. EtOH (hydrochloride, $[\alpha]_D^{25} +1.00^\circ$ in 10% HCl; d- γ -benzamidohexane, m.p. 66—68°, $[\alpha]_D^{25} +2.0^\circ$ in abs. EtOH); d- γ -nonanol, b.p. 96—98°/19 mm., $[\alpha]_D^{25} +7.08^\circ$, converted successively into l- γ -iodononane, b.p. 99—100°/10 mm., $[\alpha]_D^{25} -14.2^\circ$, d- γ -azidononane, b.p. 105—107°/30 mm., $[\alpha]_D^{25} +3.04^\circ$, d- γ -aminononane, b.p. 102°/50 mm., $[\alpha]_D^{25} +4.61^\circ$ (homogeneous), $[\alpha]_D^{25} +3.7^\circ$ in abs. EtOH (hydrochloride, $[\alpha]_D^{25} +1.5^\circ$ in H_2O ; d- γ -benzamidononane, m.p. 86°, $[\alpha]_D^{25} +12.5^\circ$ in abs. EtOH); l- δ -octanol, b.p. 79—80°/17 mm., $[\alpha]_D^{25} +0.64^\circ$, giving successively l- δ -iodooctane, b.p. 97°/22 mm., $[\alpha]_D^{25} -1.76^\circ$, l- δ -azido-octane, b.p. 92—93°/35 mm., $[\alpha]_D^{25} -0.82^\circ$, l- δ -amino-octane, b.p. 92—93°/80 mm., $[\alpha]_D^{25} +0.45^\circ$ (hydrochloride, $[\alpha]_D^{25} -0.50^\circ$ in 10% HCl; d- δ -benzamidooctane, m.p. 99—100° $[\alpha]_D^{25} +1.30^\circ$ in abs. EtOH). The rotatory dispersions of configuratively related primary and sec. amines in the homogeneous state and their corresponding hydrochlorides in H_2O are recorded. H. W.

A catalytically induced reaction [of glucosamine] resembling the Cannizzaro reaction.

P. A. LEVENE and C. C. CHRISTMAN (J. Biol. Chem., 1937, 120, 575—590).—Glucosamine (I) with H_2 (Adams' Pt) is converted, by a pseudo-Cannizzaro reaction, half into *aminosorbitol* (II) [Ac_8 derivative,



m.p. 99—100°, b.p. 160—180°/0.3 mm., $[\alpha]_D^{25} +21.0^\circ$ in CHCl_3 , converted by $\text{Ba}(\text{OMe})_2$ -MeOH into *N*-acetyl- β -aminosorbitol (IV), m.p. 152—153°, $[\alpha]_D^{25} -10.4^\circ$ in H_2O], and half into *glucosaminic acid* (III) [as (II) but with CO_2H for upper CH_2OH], $[\alpha]_D^{25} -13.4^\circ$ in 20% HCl , which is determined by titration. Slightly increased yields of (II) are obtained under high pressure of H_2 , and of (III) under atm. pressure. The reaction is unimol. until 70—80% completed. In absence of H_2 or of Pt there is no reaction. The hydrochloride of (I) with H_2 -Pt gives only *aminosorbitol*, m.p. 157—158°, $[\alpha]_D^{25} -2.4^\circ$ in 20% HCl , whilst *N*-acetylglucosamine gives (IV). In H_2 , reduced Adams' Pt converts (I) into (II) and (III), but under reduced pressure of H_2 , especially in presence of NaOH , there is almost quant. formation of (III). The mechanism of the reaction is discussed.

E. W. W.

Formation and breakdown of amino-acids by intermolecular transfer of the amino-group.

A. E. BRAUNSTEIN and M. G. KRITZMANN (Nature, 1937, 140, 503—504).—The reaction between glutamic acid (I) and AcCO_2H (II) is reversible, since these acids are rapidly formed by muscle tissue from alanine and α -ketoglutaric acid (III), and equilibrium mixtures of similar composition are obtained in both the direct and the reversed reaction. The enzyme system responsible is present in muscle, heart, brain, liver, and kidney. α -Keto-acids other than (II) can serve as acceptors for the NH_2 of (I), but, on the other hand, all α - NH_2 -acids give up their NH_2 to (III) in presence of muscle tissue; the formation of (I) with 16 different natural and racemic NH_2 -acids, including such as glycine or histidine, has been established. No transfer of NH_2 occurs unless either the NH_2 - or the keto-acid is dicarboxylic.

L. S. T.

Oxidative deamination of amino-acids. B. C. KAR (J. Indian Chem. Soc., 1937, 14, 381—387).— NH_2 -acids (glycine, leucine, alanine) are oxidised to aldehyde, CO_2 , and NH_3 by phenols in the presence of H_2O_2 and Na_2WO_4 or H_2WO_4 sol, or by quinones alone (*o*- or *p*-). Since phenols are oxidised by H_2O_2 + catalyst, the deamination must be due to quinones. Resorcinol deaminates better with H_2O_2 alone. The rate of deamination is measured by the decrease in $\text{NH}_2\text{-N}$ (Van Slyke).

A. LI.

Non-labile deuterium of amino-acids treated in dilute deuterium oxide media. J. A. STEKOL and W. H. HAMILL (J. Biol. Chem., 1937, 120, 531—536).—Treatment of *l*-cystine, arginine, histidine, and lysine with hot aq. D_2O - HCl yields products containing D in positions other than the NH_2 , NH , or CO_2H groups. Tryptic digestion of caseinogen in aq. H_2O yields tyrosine containing D in positions other than the OH , NH_2 , or CO_2H groups. The use of D in the study of NH_2 -acid metabolism is discussed.

F. O. H.

Amino-acids of the yellow enzyme. R. KUHN and P. DESNUELLE (Ber., 1937, 70, [B], 1907—1926).—Colorimetric determinations establish the presence of the following NH_2 -acids in the yellow enzyme (% in parentheses): arginine (I) (8.2), histidine (II) (2.75), lysine (III) (13.7), hydroxyproline (~ 0.0), tyrosine (7.75), phenylalanine (5.75), tryptophan (4.86), cystine (IV) (0.34), and glutamic acid (V) (7.1). As far as the method is valid, therefore, there is no fundamental difference in nature or amount between the identified NH_2 -acids and other known proteins. Only (V) has been obtained in substance (as hydrochloride). The % S in the enzyme is about thrice that required by the amount of (IV) which is present, so that other NH_2 -acids containing S must be expected. In all, account is rendered of 65% of the total N. The bases are of peculiar interest since lactoflavin-5-phosphoric acid is united to basic groups of the protein component in at least two positions, the PO_4 residue and NH at position 3. The sum of (I), (II), and (III) is very similar to that of the best known chromoprotein, haemoglobin, but the distribution is widely different. The protein of the yellow enzyme is poor in (II) but rich in (III) whereas the globin contains much (II) and little (III).

H. W.

Dipeptides of β -amino-acids. E. DYER and E. BALLARD (J. Amer. Chem. Soc., 1937, 59, 1697—1699).— $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COCl}$ and the appropriate NH_2 -acid give *N*- β -chloropropionyl-glycine, m.p. 133—135° (*Et* ester, m.p. 71—72.5°; amide, m.p. 174—175°), β -phenyl- α -alanine, m.p. 123—125°, and β -phenyl- β -alanine, m.p. 71—72.5°. $\text{CHPhBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and glycine give mainly cinnamoylglycine. None of these products give dipeptides with NH_3 . Carbobenzyloxy- β -alanyl-glycine, m.p. 145—146°, β -phenyl- α -alanine, m.p. 144.5—145°, and β -phenyl- β -alanine, m.p. 151.5—153°, with H_2 and colloidal Pd give β -alanyl-glycine, m.p. 230° (decomp.) (hydrochloride), β -phenyl- α -alanine, m.p. 264—265° (decomp.) (hydrochloride, m.p. 205.5—207°), and β -phenyl- β -alanine, m.p. 235—236° (decomp.) (hydrochloride, m.p. 180—182°), which are unchanged by HCO_2H . M.p. are corr.

R. S. C.

Biuret reaction of sarcosyldiglycine and glycylsarcosyldiglycine. J. FELDMAN (J. Amer. Chem. Soc., 1937, 59, 1657—1659).—Rising's theory of the biuret reaction is confirmed. Sarcosine anhydride gives no Cu complex. Sarcosyldiglycine (from chloroacetyldiglycine and NH_2Me), $+\text{H}_2\text{O}$, m.p. 237—239°, with $\text{Cu}(\text{OH})_2$ and NaOH in absence of CO_2 gives the complex, $\text{Na}_4\text{CuC}_{14}\text{H}_{20}\text{O}_8\text{N}_6$. Hydrogenation of carbobenzyloxyglycylsarcosyldiglycine gives glycylsarcosyldiglycine, a syrup, which affords the complex, $\text{NaCuC}_9\text{H}_{13}\text{O}_5\text{N}_4$.

R. S. C.

Protective colloids "protalbinic" and "lysalbinic" acids. S. INOUE (J. Soc. Chem. Ind. Japan, 1937, 40, 268B).—Increase in $[\text{NaOH}]$ gives acids having a decreasing N content and the Na salts have an increasing Au no. and decreasing γ which lowers the protective action (cf. Bechhold, A., 1904, ii, 650).

F. R. G.

Derivatives of aminohydroxypropanesulphonic acid. Biuret reaction. S. TSUNOO (J. Biochem. Japan, 1937, 25, 375—391; cf. A., 1935, 1111).—

The following were prepared: γ -o-, m.p. 235°, -m-, m.p. 195°, and -p-toluidino-, m.p. 247°, -m-xylydino-, m.p. 213° (decomp.), -(2-methylquinolyl)- (I), -(α -naphthylamino)-, m.p. 165–170°, -ethylamino-, -diethylamino-, -propylamino-, -allylamino-, -butylamino-, -guanido-, m.p. 225°, -(2-naphthalenesulphonylmethylamino)-, m.p. >280°, -(p-toluenesulphonamido)- (as Na salt, decomp. 260°), and -(p-toluenesulphonylmethylamino)- β -hydroxypropanesulphonic acid (as Na salt, m.p. >280°). γ -Chloro- β -hydroxypropanesulphonic acid, resolved by means of the *brucine*, m.p. 232°, and *strychnine* salts, yielded the l- (*strychnine* salt, m.p. 104–105°) and d-isomeride (*strychnine* salt, m.p. 85°), the following respective d- and l-derivatives being subsequently prepared: γ -amino-, m.p. 265°, 265°, $[\alpha]_D^{25} +9.13^\circ$, $[\alpha]_D^{20} -9.67^\circ$; -methylamino-, m.p. 223°, 225° (decomp.), $[\alpha]_D^{20} +19.86^\circ$, $[\alpha]_D^{25} -17.25^\circ$; -dimethylamino-, m.p. 251°, 243° (decomp.), $[\alpha]_D^{20} +31.96^\circ$, $[\alpha]_D^{25} -29.49^\circ$; -(n-butylamino)-, $[\alpha]_D^{20} +22.34^\circ$, $[\alpha]_D^{25} -23.08^\circ$; -trimethylamino-, m.p. >295°, 285° (decomp.), $[\alpha]_D^{20} +28.54^\circ$, $[\alpha]_D^{25} -26.63^\circ$; also the *strychnine* salt, m.p. 125°, of γ -benzamido- β -hydroxypropanesulphonic acid. All rotations are in H₂O; all m.p. uncorr. γ -Amino- β -hydroxypropanesulphonic acid, fed to rabbits, is excreted unchanged. The response of the above compounds to the ninhydrin (II) and biuret (III) reactions indicates that the group $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NRR}'$ gives both reactions when R = H and R' = alkyl, (III) but not (II) when both R and R' = alkyl, and neither reaction on betaine formation. With R or R' = aryl or with SO₂·NH₂ neither reaction is given but substitution of $\cdot\text{NH}\cdot\text{C}(\cdot\text{NH})\cdot\text{NH}_2$ for NH₂ does not inhibit (III).

F. O. H.

Ferroaminopentacyanides.—See A., I, 528.

Preparation of azomethane. F. P. JAHN (J. Amer. Chem. Soc., 1937, 59, 1761–1762).—Me₂N₂ is best obtained from NMe₂·NH₂·2HCl by conversion by CuCl₂ into Me₂N₂·Cu₂Cl₂, which is dried in vac. and heated. Me₂N₂ and Hg vapour do not explode. Explosions are caused by distilling a high-boiling oil, which is formed by oxidising old samples of the hydrazine.

R. S. C.

Improved preparations of aliphatic diazo-compounds and certain of their properties. D. W. ADAMSON and J. KENNER (J.C.S., 1937, 1551–1556).—An improved prep. of Me nitroso- β -methylaminoisobutyl ketone (cf. A., 1933, 398; 1935, 479) is described. Interaction of pulegone and the appropriate primary amine in H₂O, followed by nitrosation, yield the following: 5-methyl-2-nitroso- α -methyl-, m.p. 116.5°, -ethyl-, m.p. 108.5°, -n-propyl-, m.p. 125.5°, -n-butyl-, m.p. 89°, -n-amyl-, m.p. 88.5°, -n-heptyl-, m.p. 70°, and -allyl-isopropylcyclohexanone, m.p. 108°. From CH₂N₂ to CHPrN₂, aliphatic diazo-compounds are prepared from the appropriate Me nitroso- β -alkylaminoisobutyl ketone in PhOMe by treatment with NaO·CH₂Ph or Na cyclohexoxide under reduced pressure. Homologues higher than CHPrN₂ are similarly prepared using the NO-ketones

prepared from pulegone. The following b.p. are recorded: CHMeN₂, -19° to -17°/89.5 mm., CHEtN₂, -8° to -7.5°/41.5 mm., CHPrN₂, -3.5° to -5.5°/26 mm., CHPr^aN₂, 1° to -1°/32 mm., and the absorption spectra of these and CH₂N₂ from 2500 to 5500 Å. are measured in cyclohexanol. The reactivities of CHMeN₂, CHEtN₂, and CH₂N₂ are compared by measurement of N₂ evolution when treated with PhOH, and found to be (II) > (I) > (III). CMe₂·CHAc with (III) in Et₂O yields 5-acetyl-4:4-dimethylpyrazoline, b.p. 110°/18 mm., m.p. 51.5–52.5°, and with (I), 5-acetyl-3:4:4-trimethylpyrazoline, m.p. 76.3°, which when heated with Cu gives 2:2:3-trimethylcyclopropyl Me ketone (*semi-carbazone*, m.p. 139–140°).

J. D. R.

Phosphine and arsine derivatives of the group I(b) metals: volatile derivatives of gold. F. G. MANN and A. F. WELLS (Nature, 1937, 140, 502).—The trialkyl-phosphine and -arsine derivatives of AgI, like those of CuI, have the fourfold mol. [R₃P(As)→AgI]₄. The Ag compounds have the same constitution as the Cu⁺ compounds, since [AsPr^a₃→AgI]₄ is strictly isomorphous with [AsEt₃→CuI]₄, the effect of replacing Cu by Ag being compensated by that of Et by Pr^a; both the 4-covalent Cu⁺ and Ag⁺ atoms have a tetrahedral configuration. The aurous compounds, [R₃P(As)→AuX], where X is Cl, I, or CNS, are unimol., and the Au shows a true co-ordination no. of 2. The compounds [PR₃→AuX], where X is Cl or I, are very stable and can be freely distilled under reduced pressure. [PBU^a₃→AuCl] can be volatilised even at 1 atm., and deposits a film of Au when the vapour is passed through a heated tube.

L. S. T.

Mechanism of the reaction between sulphuric acid and mono- and di-methylarsinic acids. G. PETIT (Compt. rend., 1937, 205, 322–325).—AsMeO(OH)₂ (I) with H₂SO₄ at 315° in a sealed tube rapidly affords As₂O₃ and SO₂. At 250°, the reaction is much slower. In each case, the amount of SO₂ liberated is < that expected from the stoichiometric equation and is explained on the basis of two consecutive reactions: (a) scission of (I) to give MeOH and As(OH)₃ (which is also accomplished by H₃PO₄) and (b) oxidation of MeOH by H₂SO₄. AsMe₂·O₂H with H₂SO₄ in a sealed tube at 315° rapidly affords As₂O₃ and SO₂ in the proportions demanded by the stoichiometric equation. At lower temp., the reaction mechanism resembles that for (I). J. L. D.

Organo-magnesium compounds as reducing agents. M. MOUSSERON and R. GRANGER (Compt. rend., 1937, 204, 986–989).—The organo-magnesium derivative (I) of cyclohexylcarboxylic acid (1 part) with C₆H₁₁·MgBr (2 parts) in Et₂O in an atm. of N₂ at 0° affords cyclohexene (II), cyclohexanol (III), cyclohexylcarbinol, dicyclohexyl-methane (IV) and -carbinol, and dicyclohexyl. Two types of reaction are utilised to explain the formation of these products. The reaction is of fairly general application and is applied to straight-chain analogues of (I). cyclo-Hexylcarboxyl chloride or Et cyclohexylcarboxylate with C₆H₁₁·MgBr similarly affords dicyclohexyl ketone, (II), (III), and (IV). Aromatic aldehydes and alicyclic ketones react similarly.

J. L. D.

Preparation of stannic alkyl iodides and their action on aromatic amines. T. KARANTASSIS and C. VASSILIADIS (Compt. rend., 1937, 205, 460—462; cf. A., 1897, 918).—Prolonged interaction of Sn (2 parts) with alkyl iodides (4 parts) in a sealed tube at 130—180° affords Sn^{IV} dialkyl iodides. The following are prepared: *Sn Me*₂, m.p. 30°, *Et*₂, m.p. 42—42.5°, *Pr*₂, b.p. 166—167°/10 mm. (slight decomp.), *Bu*₂, b.p. 290—295°, and *di-isocamyl iodide*, b.p. 202—205°/8 mm. The *Me*₂ and *Et*₂ derivatives are stable at 180°, but the others decompose extensively to give, for example, *SnI*₂, *C*₃*H*₈, and propylene from *SnPr*₂*I*₂. The above iodides (1 mol.) form additive compounds with aromatic bases (2 mols.) in EtOH. The following are prepared: *SnMe*₂*I*₂ + 2*C*₅*H*₅*N*, m.p. 151—152°; + 2*NH*₂*Ph*, m.p. 109—110°; + 2*o*-*C*₆*H*₄*MeNH*₂, m.p. 69—70°; + *picoline*, liquefies in air; + 2*NPhEt*₂, m.p. 88—89°; + 2*quin-aldine*, m.p. 110—111°; *SnEt*₂*I*₂ + 2*C*₅*H*₅*N*, m.p. 115—116°; *SnPr*₂*I*₂ + 2*C*₅*H*₅*N*, m.p. 64—65°; + 2*NHPH*₂; + 2*NPhEt*₂, m.p. 63—64°; + 2*quin-aldine*, m.p. 71—72°; and *SnBu*₂*I*₂ + 2*NPhEt*₂.

J. L. D.

Theory of unsaturated and aromatic compounds. E. HÜCKEL (Z. Elektrochem., 1937, 43, 752—788).—A summary.

J. W. S.

Combustion of aromatic and alicyclic hydrocarbons.—See A., I, 522.

Bromination of bromo-, chloro-, and fluoro-benzene in the gas phase. Effect of temperature and catalyst on the substitution type. M. VAN LOON and J. P. WIBAUT (Rec. trav. chim., 1937, 56, 815—838).—The bromination of gaseous PhBr, PhCl, and PhF is investigated in an automatically functioning apparatus. In the presence of C the reaction changes at 400—450° from *o-p* to mainly *m* in all cases, a change which is inexplicable on any known theory of substitution. In the presence of FeBr₃ on C the reaction is of the *o-p* type from 200° to 500°, although the proportions of isomerides formed change considerably; these changes agree excellently for PhBr with Scheffer's equations and are determined by differences in the energies of activation which appear to be const. from 200° to 500°; differences in the entropies of activation are negligible. Mixed m.p. curves are given for *o-m*-*C*₆*H*₄ClBr, *p-o*- and *p-m*-*C*₆*H*₄BrF.

R. S. C.

Thermal polymerisation of styrene.—See A., I, 523.

β-Phenyl sulphide. IV. O. HINSBERG (Ber., 1937, 70, [B], 2027—2028; cf. this vol., 288).—β-Diphenyl sulphone (I) is converted by boiling 70% HClO₄ into β-diphenyl sulphone oxide (II), m.p. 120—122° or (+1H₂O) m.p. 82° (with a compound, m.p. 150°). (II) cannot be acetylated and is unchanged by Zn filings and boiling 20% HCl. (I) retains 0.5H₂O very obstinately.

H. W.

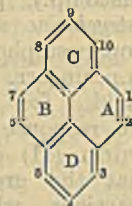
Synthesis of diradicals. pp'-Triphenylene-diphenylmethyl. E. MÜLLER and G. SOK (Ber., 1937, 70, [B], 1990—1992; cf. A., 1936, 1370).—cycloHexane-1:4-dione and LiPh in Et₂O give 1:4-diphenylcyclohexane-1:4-diol, m.p. 225°, dehydrated

and aromatised by Se at 200° to *p*-*C*₆*H*₄Ph₂ (I), m.p. 210°, in 70—80% yield. BzCl, AlCl₃, and (I) afford pp'-dibenzoylterphenyl, m.p. 294° transformed in decahydronaphthalene by LiPh in Et₂O into pp'-tetraphenylterphenylene-pp'-diol, m.p. 162°. The corresponding dichloride, m.p. 236°, when boiled with Cu-bronze in C₆H₆ gives a dark red solution, very sensitive to air. It doubtless contains the diradical. H. W.

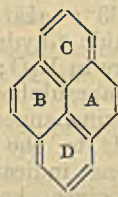
Molecular constitution of naphthalene. G. B. BONINO (Gazzetta, 1937, 67, 343—346).—A reply to Oddo on a question of priority (cf. this vol., 373).

E. W. W.

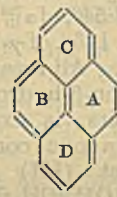
Pyrene and its derivatives. H. VOLLMANN, H. BECKER, M. CORELL, and H. STREECK [with, in part, G. LANGBEIN] (Annalen, 1937, 531, 1—159).—Monosubstitution of pyrene (I) occurs very readily and without exception in position 3. Similarly mixtures of 3:8- and 3:10-di-derivatives are invariably produced by the ready, direct disubstitution. 3:5:8-Derivatives and 3:5:8:10-compounds are formed by direct tri- and tetra-substitution. Higher substitution causes entry into the 1:2:6:7 and finally in the 4:9 positions. The behaviour of (I) towards



(Ia.)



(Ib.)



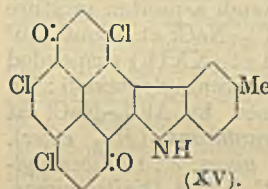
(Ic.)

substituents causes it to be regarded mainly as a Ph₂ derivative the *o*-positions of which are bridged by two ·CH·CH· residues; the mobility of H at 3, 5, 8, and 10 is attributed to the action of these residues on the typically benzenoid rings C and D. The behaviour of (I) is expressed by the formula (Ia) or (Ib) but the older formulation (Ic) is less satisfactory since it contains a *p*-quinoid nucleus A whereas (I) is colourless when pure. The assumption of an alternation of the linkings according to all these schemes accounts for the predominance of 3:10-over 3:8-di-derivatives in all cases of di-substitution.

Crude pyrene-3:8-quinone, obtained by oxidation of (I) with H₂SO₄ and K₂Cr₂O₇, is purified with difficulty by successive crystallisations from AcOH, PhCl, and PhNO₂ respectively. The pure substance is best obtained through 3:8-dihydroxypyrene or by catalytic dehalogenation of 2:5:7:10-tetrachloropyrene-3:8-quinone; the former method gives opportunity of isolating pyrene-3:10-quinone through 3:10-diacetoxypyrene, m.p. 190°. SO₂Cl₂ and (I) in CCl₄ yield 3-chloropyrene, m.p. 119°, whilst 3:5:8:10-tetrachloropyrene (II), m.p. 368°, is obtained from (I) and Cl₂ in CCl₄ at 60° or by treatment of 3:5:8:10-tetranitropyrene with PCl₅. Br and (I) in PhNO₂ at room temp. and then at 120—130° give 3:5:8:10-tetrabromopyrene (III), m.p. 402°. With oleum at 85° (II) gives 5:10-dichloropyrene-3:8-quinone, m.p. 278° (decomp.), obtained also by dehalogenation of 2:5:7:10-tetrachloropyrene-3:8-quinone. 3:5:8:10-Tetraketo-3:4:5:8:9:10-hexahydro-pyrene (naphthalene-1:8:4:5-di-indandione) (IV) is

obtained by treating (II) with oleum at 80°, diluting the solution with H₂SO₄, and raising the temp. to 200° or by the action of Zn dust and NaOH on 4:9-dibromo-3:5:8:10-tetraketo-3:4:5:8:9:10-hexahydropyrene (V) [derived from (III) and conc. H₂SO₄ at 140–150°, reduced and then oxidised to 4:9-dibromo-3:5:8:10-tetraketo-3:4:5:8:9:10-hexahydropyrene, and converted by Ac₂O containing a trace of H₂SO₄ into 4:9-dibromo-3:8-diacetoxypyrene-5:10-quinone, m.p. 270° (decomp.)]. With boiling BzCl-NPhMe₂ (IV) gives 3:5:8:10-tetrabenzoyloxypyrene, m.p. 340° (decomp.), hydrolysed to 3:5:8:10-tetrahydroxypyrene. Analogously (V) gives 4:9-dibromo-3:5:8:10-tetrabenzoyloxypyrene, m.p. >370° (decomp.). (IV) in 2% NaOH is converted by NaNO₂ and 6% H₂SO₄ into 4:9-dinitroso-3:5:8:10-tetraketo-3:4:5:8:9:10-hexahydropyrene (VI), violent decomp. >200°. 4:9-Dinitro-3:5:8:10-tetraketo-3:4:5:8:9:10-hexahydropyrene is obtained from (IV) and HNO₃ (d 1.4) or from (VI); its Na salt is reduced by Na₂S₂O₄ to 4:9-diamino-3:5:8:10-tetraketo-3:4:5:8:9:10-hexahydropyrene. (IV) suspended in dil. HCl is converted by Cl₂ into 4:4:9:9-tetrachloro-3:5:8:10-tetraketo-3:4:5:8:9:10-hexahydropyrene, decomp. >340°, which is oxidised in alkaline solution to 1:4:5:8-C₁₀H₄(CO₂H)₄. Finely divided (V) and Br at 50–70° give 4:4:9:9-tetrabromo-3:5:8:10-tetraketo-3:4:5:8:9:10-hexahydropyrene, decomp. >250°, which gives CHBr₃ when treated with alkali. Prolonged chlorination of (I) in C₆H₃Cl₃ yields 1:2:3:5:6:7:8:10-octachloro-1:2:6:7-tetrahydropyrene (VII), m.p. about 292° with evolution of HCl when rapidly heated and m.p. about 375° after re-solidification; it passes when heated at 400° into hexachloropyrene (VIII), m.p. 383° after softening at 360–370°, also obtained by use of KOH-EtOH. Treatment of (VIII) with oleum yields 2:6-, m.p. 390°, and 2:7-, m.p. 296°, -dichloronaphthalene-tetracarboxylic dianhydride; the last-named is also obtained from 3:8-dichloroacenaphthene-5:6-dicarboxylic acid, the anhydride, m.p. 289° after darkening at 275°, of which is described. The mother-liquors from the prep. of (VII) contain 1:2:3:5:6:7:8:10-octachloropyrene (IX), m.p. 238°. Treatment of (VIII) with Cl₂ and I in ClSO₃H gives perchlorohydropyrene, decomp. about 260°, and decachloropyrene (X), m.p. 264°, converted by 20% oleum at 110° followed by H₂SO₄ and HNO₃ at 180° into 2:3:6:7-tetrachloronaphthalenetetracarboxylic dianhydride, m.p. >400° after darkening at 350°. Oxidation of (VIII) with HNO₃ (d 1.5) at +5° yields 2:5:7:10-tetrachloropyrene-3:8-quinone, m.p. 320–325° after darkening at 310°. Similar treatment of (IX) affords 1:2:5:6:7:10-hexachloropyrene-3:8-quinone, m.p. 274°, whilst (X) yields 1:2:4:5:6:7:9:10-octachloropyrene-3:8-quinone, m.p. 304°. 4:5:9:10-Tetrachloro-4:5:9:10-tetrahydropyrene-3:8-quinone, from the 3:8-quinone and Cl₂ in C₆H₃Cl₃ at 100°, passes when distilled with steam into 4:9-dichloropyrene-3:8-quinone (XI), m.p. >500° after darkening at 330°. 5-Chloropyrene-3:8-quinone, m.p. 248°, obtained by use of SO₂Cl₂ in PhNO₂ at 100°, and 4:5:9:10-tetrachloropyrene-3:8-quinone, m.p. 377°, prep. by chlorination in C₆H₃Cl₃ at 150–170°, are described. Chlorination of 3:8-

dimethoxypyrene (XII) with SO₂Cl₂ in C₆H₃Cl₃ containing CaCO₃ at 150° yields 5:10-dichloro-3:8-dimethoxypyrene, m.p. 279°, also obtained by the action of Me₂SO₄ and NaOH on 5:10-dichloro-3:8-dihydropyrene, decomp. >350°, prep. by reducing the corresponding quinone with NPh-NH₂ in C₆H₃Cl₃. Treatment of (XII) in PhCl with SO₂Cl₂ and dioxan gives 5-chloro-3:8-dimethoxypyrene, m.p. 315°. Reduction of (XI) in C₆H₃Cl₃ by NPh-NH₂ at 130–140° gives 4:9-dichloro-3:8-dihydropyrene, m.p. 274°, whence 4:9-dichloro-3:8-dimethoxypyrene, m.p. 256°. 5-Nitropyrene-3:8-quinone has m.p. 335° (decomp.). (XII) and HNO₃ (d 1.4) in boiling AcOH afford 5:10-dinitro-3:8-dimethoxypyrene (XIII), m.p. 357° (decomp.), whilst addition of NaNO₂ to (XII) in boiling PhCl containing AcOH yields 5-nitro-3:8-dimethoxypyrene, m.p. 237°, catalytically reduced to 5-amino-3:8-dimethoxypyrene, m.p. 255°, and oxidised by HNO₃ to (XIII). The tetrachloroquinone is converted by NH₂Ph at 50°, by cryst. NaOAc and NH₂Ph at 130–140°, and by boiling NH₂Ph containing Cu powder into 3:6:8-trichloro-1-anilinopyrene-5:10-quinone, m.p. 269–270°, 3:8-dichloro-1:6-dianilinopyrene-5:10-quinone (XIV), m.p. 335°, and 1:3:6:8-tetra-anilinopyrene-5:10-quinone, m.p. 390–395°, respectively, and by anhyd. KOAc in boiling PhNO₂ followed by boiling dil. AcOH into 3:6:8-trichloro-1-hydropyrene-5:10-quinone, m.p. 322° (decomp.) (Na salt), by NH₃ at 120° into 3:6:8-trichloro-1-aminopyrene-5:10-quinone, m.p. >350° (decomp.) (Bz derivative, m.p. 323°), and by p-C₆H₄Me-NH₂ and NaOAc in boiling PhCl into 3:6:8-trichloro-1-p-toluidinopyrene-5:10-quinone, m.p. 297°

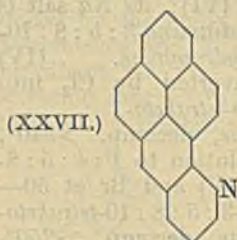


[whence the carbazole derivative (XV)]; (XIV) yields the analogous dicarbazole compound, m.p. 338°. 2:6-C₁₀H₆(OBz)₂ with NaCl-AlCl₃ at 155–200° gives 1:6-dihydroxy-3:4:8:9-dibenzopyrene-5:10-quinone (XVI), m.p. >450° [corresponding Me₂ derivative (XVII), m.p. 360° (decomp.)]. (XVI) with PCl₅ in boiling PhCl yields a keto-chloride, hydrolysed by conc. H₂SO₄ at 100° to 1:6-dichloro-3:4:8:9-dibenzopyrene-5:10-quinone, m.p. >400°, or, under other conditions, into 1:5:6:10-tetrachloro-3:4:8:9-dibenzopyrene, m.p. about 336° after softening at 300°. (XVI) or (XVII) with boiling p-C₆H₄Me-NH₂ affords 1:6-di-p-toluidino-3:4:8:9-dibenzopyrene-5:10-quinone, m.p. 379–380°. 2:6-Dichloro-, m.p. 400°, and 2:6-dianilino-, m.p. 400°, -naphthalene-1:4:5:8-tetracarboxydi-phenylimide are described.

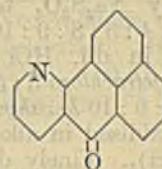
ClSO₃H and (I) in CCl₄ at 0–5° yield pyrene-3-sulphonic acid [Na salt (XVIII), converted by PCl₅ in POCl₃ into the corresponding chloride, m.p. 120° (decomp.)]. 3-Hydropyrene, m.p. 179° (Ac derivative, m.p. 102°; Me ether, m.p. 93°), from (XVIII) and NaOH at 270–290°, does not couple with diazotised aromatic amines. 3-Nitropyrene (XIX), m.p. 153–154°, is obtained from (I) and HNO₃ (d 1.4) in AcOH at 50°. Successive addition of POCl₃ and (I) to formylmethylaniline in o-C₆H₄Cl₂ leads to pyrene-3-aldehyde, m.p. 126° (phenylhydrazone, m.p. 201–202°). 3-Acetylpyrene (XX), m.p. 90°, is

obtained from (I) and ZnCl_2 in $\text{AcOH}-\text{Ac}_2\text{O}$ at 80° . 3-Benzoylpyrene (XXI) gives an *oxime*, m.p. 220° , isomerised by PCl_5 in C_6H_6 to *pyrene-3-carboxyanilide*, m.p. 255° . Reduction of (XIX) by NaSH in $\text{EtOH}-\text{H}_2\text{O}$ yields 3-aminopyrene, m.p. $117-118^\circ$ (*Ac* derivative, m.p. 260°). 3-Chloropyrene is transformed by CuCN at $300-340^\circ$ into 3-cyanopyrene, m.p. 153° , hydrolysed by aq. NaOH at 180° to *pyrene-3-carboxylic acid*, m.p. 274° (corresponding *chloride*, m.p. 152° , and *anilide*, m.p. 255°), also obtained by oxidising (XX) in boiling $\text{C}_5\text{H}_5\text{N}$ by aq. NaOCl . (XXI) with $\text{AlCl}_3-\text{NaCl}$ at $160-165^\circ$ gives 2:3(CO)-benzoylenepyrene, m.p. 242° ; this with molten KOH at $170-245^\circ$ gives 1-phenylpyrene-o-carboxylic acid, m.p. 218° , converted by dry distillation of the *Ba* salt into 1-phenylpyrene, m.p. 169° . $\text{CH}_2\text{Cl}-\text{CO}_2\text{H}$ and (I) in $o\text{-C}_6\text{H}_4\text{Cl}_2$ at $180-190^\circ$ yield *pyrenyl-3-acetic acid*, m.p. 220° (decomp.), which when distilled with $\text{NaOH}-\text{CaO}$ affords 3-methylpyrene, m.p. $71-72^\circ$ (*picrate*, m.p. $211-212^\circ$), obtained also from pyrene-3-aldehyde and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 200° . Distillation of (XX) with Zn dust gives 3-ethylpyrene, m.p. $94-95^\circ$. Gradual addition of $\text{CH}_2\text{Cl}-\text{COCl}$ to (I) and AlCl_3 in CS_2 gives 3:8-, m.p. 288° , and 3:10-, m.p. 202° , -dichloroacetylpyrene, oxidised by NaOCl in $\text{Bu}^n\text{OH}-\text{EtOH}-\text{H}_2\text{O}$ at 90° to *pyrene-3:8-dicarboxylic acid*, m.p. $>365^\circ$ (decomp.) [corresponding *chloride* (XXII), m.p. 262°], and *pyrene-3:10-dicarboxylic acid*, m.p. $>365^\circ$ (decomp.) [*chloride* (XXIII), m.p. 235°]. With C_6H_6 and AlCl_3 (XXII) gives 3:8- (XXIV), m.p. 239° , and (XXIII) gives 3:10- (XXV), m.p. 165° , -dibenzoylpyrene, the mixture of which is obtained from (I), AlCl_3 , and BzCl in CS_2 at room temp. Passage of dry O_2 through a molten mixture of (XXIV) or (XXV) with $\text{AlCl}_3-\text{NaCl}$ at about 120° gives pyranthrone. Oxidation of (XXIV) suspended in AcOH by CrO_3 yields 3:8-dibenzoylpyrene-5:10-quinone, m.p. 292° , transformed by $\text{AlCl}_3-\text{NaCl}$ at $140-150^\circ$ into *dihydroxypyranthrone* (*Me*, ether). Similar oxidation of (XXV) gives 3:10-dibenzoylpyrene-5:8-quinone, m.p. 242° . 3:8-Dinitropyrene, m.p. 309° , is obtained mixed with the 3:10-isomeride by the addition of HNO_3 (*d* 1.4) to (I) in AcOH at 90° ; reduction of the mixture by NaSH in $\text{EtOH}-\text{H}_2\text{O}$ leads to 3:8-diaminopyrene, m.p. $232-233^\circ$ (*sulphate*; *Ac*, derivative, m.p. about 410° after blackening at about 375°), and 3:10-diaminopyrene, m.p. $160-162^\circ$ (*Ac*, derivative, decomp. about 350°). Nitration of 3-acetamidopyrene gives a mixture, reduced (*Na* in EtOH) and separated into 3-amino-8-, m.p. 280° , and 3-amino-10-, m.p. $250-251^\circ$, -acetamidopyrene. 3:5:8:10-Tetranitropyrene, m.p. 332° , is described. KCN and (III) in boiling $\text{CH}_2\text{Ph}-\text{CN}$ yield 3:5:8:10-tetracyanopyrene, m.p. about 450° , hydrolysed by 10% NaOH at 180° to *pyrene-3:5:8:10-tetracarboxylic acid* (*Et*, ester, m.p. 194°), the *tetrachloride*, m.p. 226° , of which is transformed by C_6H_6 and AlCl_3 in CCl_4 into 3:5:8:10-tetra-benzoylpyrene, m.p. 282° . 3:5:8:10-Tetrachloropyrene, m.p. $299-300^\circ$, from (II), AlCl_3 , and C_6H_6 , is oxidised by CrO_3 in AcOH to 1:4:5:8-tetra-benzoylnaphthalene, m.p. 373° , which is very stable towards further oxidation. 2:3:3':2'-Dipyrenylene has m.p. $212-214^\circ$. (I), $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, and AlCl_3 in C_6H_6 yield *o-3-pyrenylbenzoic acid*, m.p. $225-$

226° , which with BzCl in boiling $1\text{-C}_{10}\text{H}_7\text{Cl}$ gives 3:4-phthaloylpyrene, m.p. 254° . Diphthaloylpyrene, m.p. $>420^\circ$, is described. β -3-Pyrenoylpropionic acid, m.p. 184° , is reduced by Zn dust and NaOH to γ -3-pyrenylbutyric acid, m.p. 184° , transformed by the successive action of PCl_5 and AlCl_3 in C_6H_6 into 3:4:4'-keto-1':2':3':4'-tetrahydrobenzpyrene, m.p. 171° , and thence by distillation with Zn dust into 3:4-benzpyrene (XXVI), m.p. 175° . 3:4:8:9-Dibenzpyrene has m.p. 316° . Oxidation of (XXVI) by CrO_3 yields 3:4-benzpyrene-5:8-quinone, m.p. 245° (corresponding *quinol diacetate*, m.p. 204°), and 3:4-benzpyrene-5:10-quinone, m.p. 295° (corresponding *quinol diacetate*, m.p. 242°). Under other conditions (XXVI) affords benzanthroneperidicarboxylic anhydride, m.p. $364-365^\circ$. Treatment of (XIX) with 3-aminopyrene, glycerol, and conc. H_2SO_4 leads to 3:4-pyridinopyrene (XXVII), m.p.



(XXVII.)



(XXVIII.)

157° , oxidised to 3:4-pyridinopyrene-5:10-quinone, m.p. 330° , converted by NaOCl in boiling $\text{C}_5\text{H}_5\text{N}$ into 11-azabenzanthroneperidicarboxylic acid [the corresponding *anhydride*, m.p. 349° , is converted by $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ into a *benzimidazole* derivative], the *Ba* salt of which passes into 11-azabenzanthr-7-one (XXVIII), m.p. $159-160^\circ$. Et_2 3-pyrenylidenemalonate, m.p. 114° , from the aldehyde and $\text{CH}_2(\text{CO}_2\text{Et})_2$ in boiling Ac_2O , is hydrolysed to 3-pyrenylidenemalononic acid, decomp. about 230° (3-pyrenylacrylic acid, m.p. 270°), transformed by ZnCl_2 in Ac_2O into *pyreneindenonecarboxylic acid* (XXIX), decomp. $302-303^\circ$; this yields 1:8:9-naphthanthrene (XXX), m.p. 135° , also obtained by the



(XXIX.)



(XXX.)

distillation of 1:8:9-naphthanthrone (XXXI) with Zn dust. (XXX) or (XXXI) is oxidised by CrO_3 in AcOH to 1:8:9-naphthanthrone-10-naphtha-1:2-quinone, m.p. 378° (decomp.) [corresponding *phenazine* derivative, m.p. (indef.) 352°]. *Pyrene-4-carboxylic acid*, m.p. 326° (*Me*, m.p. 136° , and *Et*, m.p. 117° , ester; corresponding *chloride*, m.p. 166°), is converted into the corresponding *hydrazide*, m.p. 230° and m.p. (indef.) $>300^\circ$ after re-solidification (*Ac* derivative, m.p. 290° (decomp.)); *di-4-pyrenylhydrazine*, m.p. $368-369^\circ$, which is transformed through the *azide* and 4-acetamidopyrene, m.p. 229° , into 4-aminopyrene (XXXI), m.p. 207° . 3-Aminopyrene sulphate passes in boiling $o\text{-C}_6\text{H}_4\text{Cl}_2$ into

3-aminopyrene-4-sulphonic acid, the Na salt (XXXII) of which is converted by NaOH at 160° into **4-hydroxypyrene**, m.p. 206—207° (acetate, m.p. 114°; Me ether, m.p. 105—106°), also obtained from (XXXI) (Sandmeyer); it couples with diazotised aromatic amines. (XXXII) is converted into the corresponding hydrochloride, which gives **3-cyanopyrene-4-sulphonic acid** (Na salt; corresponding chloride, m.p. 265°) when diazotised and treated with $K_3Cu(CN)_4$. **Pyrene-4-carboxylamide** and PCl_5 in $C_6H_5Cl_3$ give **4-cyanopyrene**, m.p. 203—204°, also obtained by distilling Na pyrene-4-sulphonate with KCN; it is converted by N_2H_4 , H_2O at 200° into **4-methylpyrene**, m.p. 143—143.5° (picrate, m.p. 192°). Under differing conditions hexahydropyrene (XXXIII) is transformed by Br into **1-bromo-**, m.p. 130—131°, and **1:6-dibromo-**, m.p. 194°, -3:4:5:8:9:10-hexahydropyrene (XXXIV). (XXXIII) and SO_2Cl_2 containing a little $AlCl_3$ yield **1:6-dichloro-3:4:5:8:9:10-hexahydropyrene**, m.p. 182—183°. $ClSO_3H$ and (XXXIII) in $PhNO_2$ at 16—25° give **hexahydropyrene-1-sulphonic acid** whereas the **1:6-disulphonic acid** is obtained from (XXXIII) and conc. H_2SO_4 at room temp.; the corresponding Na salts did not give satisfactory results when fused with NaOH. **1-Acetyl-**, m.p. 85—86°, and **1:6-diacetyl-**, m.p. 182°, -hexahydropyrene are oxidised by NaOCl in presence of C_5H_5N to **hexahydropyrene-1-**, m.p. 241° (Na salt), and **-1:6-di-**, m.p. 322° (decomp.), -carboxylic acid. **1-Benzoyl-**, m.p. 109°, and **1:6-dibenzoyl-**, m.p. 275°, -hexahydropyrene are described; the latter did not undergo ring-closure satisfactorily when fused with $AlCl_3$ -NaCl in presence of O_2 . CuCN and boiling (XXXIV) yield **1:6-dicyanohexahydropyrene** (XXXV), m.p. 303°, whereas at 320—350° they give **pyrene-1:6-dinitrile**, m.p. 406°, also obtained by dehydrogenating (XXXV) with Se in boiling ethylcarbazole. **Pyrene-1:6-dicarboxylic acid**, decomp. about 420°, is converted by PCl_5 in $C_6H_5Cl_3$ at 170—180° into the corresponding dichloride, which with C_6H_6 and $AlCl_3$ affords **1:6-dibenzoylpyrene** (XXXVI), m.p. 237°, and (?) **1-benzoylpyrene-6-carboxylic acid**, m.p. 252°. Oxidative treatment of (XXXVI) with $AlCl_3$ -NaCl at 140—150° leads to **1:10:6:5-dibenzoylenepyrrene**. Ozonisation of (I) in AcOH gives **4-aldehydophenanthrene-5-carboxylic acid** (XXXVII), m.p. 276°, oxidised by CrO_3 in AcOH at 80° to **phenanthrene-4:5-dicarboxylic acid**, m.p. 298° (decomp.) (corresponding azine, m.p. 330°, and its anhydride, m.p. 340°). Oxidation of (XXXVII) by $KMnO_4$ in alkaline solution gives **diphenyl-2:2':6:6'-tetracarboxylic acid**, m.p. about 390° (decomp.), converted by heating with $Cu(OAc)_2$ into Ph_2 and fluorenone.

2-Amino-1-hydroxypyrene, decomp. 250°, obtained by reduction of **2-benzeneazo-1-hydroxypyrene**, m.p. 197°, is oxidised by CrO_3 to **pyrene-1:2-quinone** (XXXVIII), m.p. 310° (corresponding azine, m.p. 262°), also obtained by fusion of (XXXVII) with KOH. Oxidation of (XXXVIII) with CrO_3 in AcOH at 90° gives **pyrene-1:2:6:7-di-quinone**, m.p. about 365° (decomp.), which affords a **diphenazine** derivative, m.p. >420°. **1-Hydroxypyrene** (XXXIX), m.p. 206—207° (Ac derivative, m.p. 113—114°), is prepared from (XXXVII) and $N_2H_4 \cdot H_2O$ in boiling

AcOH or by the energetic reduction of (XXXVIII). It is converted by aq. $(NH_4)_2SO_3$ at 150° into **1-aminopyrene**, m.p. 182° (hydrochloride; sulphate; Ac derivative, m.p. 276°). Glycerol, 80% H_2SO_4 , and (XXXIX) at 120—125° give **1:8:9-naphth-anthr-10-one**, m.p. 243°, also obtained similarly from (I). H. W.

Polyterpenes and polyterpenoids. CXV. **Synthesis of 1:8-dimethyl- and 2-methoxy-1:8-dimethyl-picene and their identification with the products of the dehydrogenation of pentacyclic triterpenes.** L. RUZICKA and K. HOFMANN [with H. BAUER, P. MÜLLER, G. RUFFONI, and P. RUSCONI] (Helv. Chim. Acta, 1937, 20, 1155—1164).—1-Keto-7-methyl-1:2:3:4-tetrahydronaphthalene is converted by Zn and $CH_2Br \cdot CO_2Et$ in C_6H_6 into **Et 7-methyl-3:4-dihydro-1-naphthylacetate**, b.p. 112—122°/0.4 mm., reduced by Na and EtOH to **β-7-methyl-1:2:3:4-tetrahydro-1-naphthylethyl alcohol**, b.p. 115—118°/0.1 mm., whence the corresponding bromide (I), b.p. 104—105°/0.1 mm. The Mg derivative of this reacts with **1-keto-5-methyl-1:2:3:4-tetrahydronaphthalene**, b.p. 143—145°/10 mm., m.p. 49—50°, to form **α-7-methyl-1:2:3:4-tetrahydro-1-naphthyl-β-5'-methyl-3':4'-dihydro-1'-naphthylethane**, b.p. 185—186°/0.1 mm., dehydrogenated (Pd-C at 320°) to **α-7-methyl-1-naphthyl-β-5'-methyl-1'-naphthylethane**, which after purification through Al_2O_3 (Brockmann) has m.p. 74—75°. It is transformed by $AlCl_3$ in CS_2 at room temp. into **1:8-dimethylpicene**, m.p. 305—306°, identical with that derived from gypsogenin, hederagenin, quinoic acid, ursolic acid, friedelinol, and β-amyrene. Condensation of $CHNa(CO_2Et)_2$ with ω-chloro-3-methoxy-2-methylacetophenone gives the corresponding malonate, b.p. 140—150°/0.5 mm., hydrolysed and decarboxylated to **γ-keto-γ-3-methoxy-o-tolylbutyric acid**, m.p. 130—130.5°. This is reduced (Clemmensen) to **γ-3-methoxy-o-tolylbutyric acid**, b.p. 144—145°/0.1 mm., m.p. 109—110°, cyclised by successive treatments with $SOCl_2$ and $AlCl_3$ in CS_2 to **1-keto-6-methoxy-5-methyl-1:2:3:4-tetrahydronaphthalene**, b.p. 123—124°/0.1 mm., m.p. 114—115°. This is transformed by the Grignard compound from (I) into **α-6-methoxy-5-methyl-3:4-dihydro-1-naphthyl-β-7'-methyl-1':2':3':4'-tetrahydro-1'-naphthylethane**, b.p. 197—198°/0.02 mm., dehydrogenated to **α-6-methoxy-5-methyl-1-naphthyl-β-7'-methyl-1'-naphthylethane**, m.p. 121—122°, which is cyclised by $AlCl_3$ in CS_2 to **2-methoxy-1:8-dimethylpicene**, m.p. 358—359°, identical with that derived from amyren. H. W.

Aromatic nitro-derivatives. X. Naphthalene derivatives. A. MANGINI and B. FRENGUELLI. **XI. Action of some diamines on 1-chloro-2:4-dinitronaphthalene.** A. MANGINI (Gazzetta, 1937, 67, 358—370, 373—380).—X. The structure of substituted $C_{10}H_6$ derivatives is discussed on Bonino's theory (A., 1935, 1057), and extended to substituted naphthalenes. The rate of reaction of **1:2:4- $C_{10}H_5Cl(NO_2)_2$** (I) with NH_2Ph and other amines is studied: it is always > that of **1:2:4- $C_{10}H_5Cl(NO_2)_2$** . The following are described: **N-4-diphenyl-**, m.p. 174—174.5°, **-p-bromophenyl-**, m.p. 223.5—224.5°, **-p-carboxyphenyl-**, m.p. 269—270° (decomp.), **-p-**

carbethoxyphenyl-, m.p. 146.5—148°, and -*p*-hydroxyphenyl-2':4'-dinitro-1'-naphthylamine, m.p. 219.5—220.5°; and 4-(2':4'-dinitroanilino)diphenyl, m.p. 144—145°.

XI. With diamines (I) gives compounds of type $\text{NH}_2 \cdot \text{R} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_5(\text{NO}_2)_2$ or type $\text{R}[\text{NH} \cdot \text{C}_{10}\text{H}_5(\text{NO}_2)_2]_2$, according to reactivity and proportion of amine used. The following are described: N-*o*-, m.p. 177.5—178° [hydrochloride; Ac derivative, m.p. 218—219° (decomp.)], N-*m*-, m.p. 195—196° (decomp.) (Ac derivative, m.p. 205—206°), and N-*p*-aminophenyl-2':4'-dinitro-1'-naphthylamine, m.p. 232—233° (decomp.) (Ac derivative, m.p. 245—246°); and NN'-bis-(2':4'-dinitro-1'-naphthyl)-*m*-, m.p. 252—253° (decomp.), and -*p*-phenylenediamine, m.p. > 290°. 2:4'- $\text{NH}_2[\text{C}_6\text{H}_4]_2\text{NH}_2$ gives a mixture from which only NN'-bis-(2':4'-dinitro-1'-naphthyl)-2:4'-diaminodiphenyl, m.p. < 290°, is isolated. Benzidine yields N-2':4'-dinitro-1'-naphthylbenzidine, m.p. 228.5—229.5° (Ac derivative, m.p. 205—206.5°), and NN'-bis-(2':4'-dinitro-1'-naphthyl)benzidine, m.p. < 290°. $(\text{CH}_2 \cdot \text{NH}_2)_2$ yields NN'-bis-(2:4-dinitro-1-naphthyl)-ethylenediamine, m.p. 170°, resolidifying to melt again at 250—260° (variable), converted by Ac_2O into N-β-acetamidoethyl-2:4-dinitro-1-naphthylamine, m.p. 162—163°. E. W. W.

Condensation products of the diphenylamine series [methylsulphonyldiphenylamines].—See B., 1937, 885.

cis-Form of azobenzene. G. S. HARTLEY (Nature, 1937, 140, 281).—The *cis*-form of azobenzene has been separated by extraction of a COMe_2 solution, which has been exposed to light, with H_2O , and extraction of the aq. extract with CHCl_3 after treatment with light petroleum. The m.p. is at least 2° > that of the normal form; the absorption coeff. for blue light is greater, and the dipole moment in C_6H_6 is 3.0 D units. Equilibrium is attained under the usual conditions with approx. 27% of the *cis*-form. L. S. T.

Decomposition of benzenediazonium chloride. W. A. WATERS (Nature, 1937, 140, 466—467).—When suspended in an org. liquid, PhN_2Cl (I) appears to melt at approx. 50° with violent decomp. HCl is often formed and is always accompanied by PhCl . In COMe_2 with excess of CaCO_3 , the chief reaction is $(\text{I}) + \text{COMe}_2 = \text{N}_2 + \text{C}_6\text{H}_6 + \text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{Me}$. Free neutral radicals are supposed to be formed as (I) decomposes. When this decomp. in $\text{COMe}_2 + \text{CaCO}_3$ is carried out in presence of Sb, Bi, Pb, or Hg, the metal is rapidly attacked at room temp.; with Hg, HgPhCl is formed. L. S. T.

"Catalytically polar" materials.—See A., I, 523.

[Metallic salts of] diazoamino-compounds. IV. A. MANGINI (Gazzetta, 1937, 67, 384—388; cf. A., 1935, 969).—2:2'-(I), 3:3'-(II), and 4:4'-dinitro-(III), and 4:4'-dimethyl-(IV), and 4:4'-dibromo-diazoaminobenzene (V) give salts as follows: (I) and (II), intensely coloured *K* salts; (II) and (III), *Ag* salts in yellow, orange, and red forms; (IV) and (V), yellow *Ag* salts; and (II), yellow, and (III), orange-yellow and red, *Hg* salts. The *Hg* salts of

(IV) and (V) are obtained in yellow forms only, but these give red solutions in PhNO_2 . E. W. W.

Refractive indices of aniline-*o*-chlorophenol mixtures and the nature of the molecular compound. C. D. ELLYETT (Trans. Faraday Soc., 1937, 33, 1212—1217).—The vals. of n_D^{20} have been determined for $\text{NH}_2\text{Ph} \cdot \text{o-C}_6\text{H}_4\text{Cl} \cdot \text{OH}$ mixtures. The departures of the mol. refractivity from the mixture law are within experimental error. Trew's results (A., 1932, 801) for $\text{CHBr}_3 \cdot \text{COMe}_2$ mixtures are recalc. The conclusion of Smyth *et al.* (A., 1929, 994) that in such cases only dipole association occurs is criticised and a resonance link is proposed. It is considered to be most probable that in the intermediate compound the N of the NH_2Ph is linked to the phenolic H of the *o*- $\text{C}_6\text{H}_4\text{Cl} \cdot \text{OH}$ mol. This is supported by the fact that the large heat of mixing, and therefore the compound formation, disappears when the OH is replaced by H or OMe. The existence of a chelate ring in *o*- $\text{C}_6\text{H}_4\text{Cl} \cdot \text{OH}$ is discussed. J. W. S.

Heats of reaction and specific heats of aniline-*o*-chlorophenol mixtures.—See A., I, 507.

Thermal decomposition of cresol on a glowing wire. K. PETERS and K. WINZER (Brennstoff-Chem., 1937, 18, 357).—The reactions occurring when cresol (b.p. 190—210°) was decomposed by immersing in it an electrically-heated wire (cf. B., 1936, 133) can be represented approx. by: $30\text{C}_6\text{H}_4\text{Me} \cdot \text{OH} = 15\text{C}_6\text{H}_6 + 5\text{PhMe} + \text{Ph}_2 + 30\text{CO} + 15\text{CH}_4 + 20\text{H}_2 + 28\text{C}$. The rate of decomp. of cresol is \ll that of paraffin hydrocarbons under similar conditions.

A. B. M.

Pyrolysis of 2:4:6-trialkylphenyl allyl ethers. C. D. HURD and W. A. YARNALL (J. Amer. Chem. Soc., 1937, 59, 1686—1690).—Diallyl and $\text{CH}_2\text{:CHMe}$, but not allene, are evolved during pyrolysis of Ph allyl ethers; the rearrangement is in part intermol. *p*-Tolyl allyl ether (modified prep.), b.p. 97—98°/16 mm., gives 69% of 3-allyl-*p*-cresol (I), b.p. 115—118°/14 mm. (gives 3-allyl-*p*-tolylloxyacetic acid, m.p. 124—125°), and a little *p*-cresol and 3:5-diallyl-*p*-cresol (II), b.p. 134—141°/15 mm., hydrogenated to 3:5-diisopropyl-*p*-cresol (III), b.p. 138—142°/17 mm., m.p. 21° (3:5-dinitrobenzoate, m.p. 96°). 1:3:4- $\text{C}_6\text{H}_3\text{MePr}^n \cdot \text{OH}$, prepared by hydrogenation of (I) (gives 3-propyl-*p*-tolylloxyacetic acid, m.p. 114—115°), gives an allyl ether, b.p. 123—124°/16 mm., which at 230—275° affords 67% of 3-propyl-5-allyl-*p*-cresol, b.p. 135°/13 mm. [hydrogenated to (III)], with 24% of (I). The allyl ether, b.p. 148°/15 mm., of (II) at 250—270° gives diallene, (III), and $\text{CH}_2\text{:CHMe}$.

R. S. C.

Nitrated *o*-alkyl-phenolic compounds.—See B., 1937, 878—879.

Introduction of the triphenylmethyl group. II. III. Mobility of the bromine atom in triphenylmethylisochavibetol and its derivatives. I. E. FUNAKUBO (Ber., 1937, 70, [B], 1981—1982, 1983—1986; cf. A., 1936, 1388).—II. *iso*-Chavibetol is converted by short heating with CPh_3Cl in $\text{C}_5\text{H}_5\text{N}$ at 155° into the oxonium salt, which passes into *isochavibetol* CPh_3 ether (the yield of which attains its max. in 10 hr. and then slowly

declines) and triphenylmethylisochavibetol [2-methoxy-6-triphenylmethyl-5- Δ^6 -propenylphenol] (I) max. production of which is observed after 40 hr. The product of the action of HI on (I) is 1:2-dihydroxy-3-triphenylmethyl-4-propylbenzene, m.p. 93—96°.

III. The presence of $\cdot\text{CPh}_3$ confers mobility on α -Br. Addition of Br to (I) in Et_2O gives the corresponding dibromide (II), m.p. 128° (decomp.) when freshly prepared or decomp. 155° after preservation or crystallisation from light petroleum. (II) is transformed by short boiling with MeOH into 2-methoxy-6-triphenylmethyl-5- β -bromo- α -methoxy-*n*-propylphenol (III), m.p. 184.5° (decomp.), and by boiling EtOH into the corresponding α -ethoxy-compound, m.p. 174° (decomp.). Br and triphenylmethylisochavibetol Me ether in Et_2O at 15° afford 2-methoxy-6-triphenylmethyl-5- $\alpha\beta$ -dibromopropylanisole, m.p. 150.5—151° (decomp.), converted by MeOH into 2-methoxy-6-triphenylmethyl-5- β -bromo-2-methoxy-*n*-propylanisole, m.p. 172—172.5° (decomp.) [also obtained by methylation (Me_2SO_4) of (III)], and by EtOH into the corresponding α -OEt-compound, m.p. 159—160° (decomp.). Indications of the replacement of β -Br are not observed and isochavibetol dibromide and its Me ether are stable under these treatments. H. W.

System: pyrogallol-*p*-phenylenediamine.—See A., I, 517.

Pentahydroxybenzene series. I. G. AULIN and H. ERDTMAN (Svensk Kem. Tidskr., 1937, 49, 208—215).—2:6-Dimethoxybenzoquinone with Br in CHCl_3 in the cold affords 4:6-dibromo-2:5-dihydroxy-1:3-dimethoxybenzene, m.p. 140.5—142.5° (diacetate, by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$, m.p. 103—104°), whilst at 100°, 3:5-dibromo-2:6-dimethoxy-1:4-benzoquinone (I), m.p. 174.5—176.5°, is formed. (I) with MeOH-NaOH affords 6-bromo-2:5-dihydroxy-3-methoxy-1:4-benzoquinone (II), decomp. 203—205°, converted by $\text{Zn}-\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ into 6-bromo-3-methoxy-1:2:4:5-tetra-acetoxybenzene (III), m.p. 165—166.5°, and reduced ($\text{Pd}-\text{H}_2$) to 2:5-dihydroxy-3-methoxy-1:4-benzoquinone, m.p. 158—160°. 3-Methoxy-1:2:4:5-tetra-acetoxybenzene, m.p. 182—182.5°, obtained in the same manner as (III), is hydrolysed ($\text{MeOH}-\text{H}_2\text{SO}_4$) and methylated (Me_2SO_4 -NaOH) to pentamethoxybenzene, m.p. 59—60°. 1:2:3:4- $\text{C}_6\text{H}_2(\text{OMe})_4$ with Br in CHCl_3 affords 5:6-dibromo-1:2:3:4-tetramethoxybenzene, b.p. 153—155°/0.6 mm., oxidised (HNO_3) to 5:6-dibromo-2:3-dimethoxybenzoquinone, m.p. 126—127°, which is hydrolysed (NaOH) to (II). J. D. R.

Alkanolamines. II. Reaction of the chloronitrobenzenes with monoethanolamine. C. B. KREMER (J. Amer. Chem. Soc., 1937, 59, 1681—1682; cf. A., 1936, 485).— o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, $\text{NH}_2\cdot[\text{CH}_2]_2\text{OH}$, and Na_2CO_3 give 60—70% of *N*- β -hydroxyethyl-*o*-nitroaniline, m.p. 76°, and 5—8% of o - $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$; $\text{Sn}-\text{HCl}$ affords *N*- β -hydroxyethyl-*o*-phenylenediamine, m.p. 107°. *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ gives 15—20% of *N*- β -hydroxyethyl-*p*-nitroaniline, m.p. 111—111.5°, with 5—8% of *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ and 15—20% of (*p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}$) $_2$. *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ gives only 50—60% of *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ and 30—40% of (*m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}$) $_2$. R. S. C.

Some bases of physiological interest. H. C. BHATNAGAR, N. N. CHOPRA, K. S. NARANG, and J. N. RAY (J. Indian Chem. Soc., 1937, 14, 344—348).— $\text{NMe}_2\cdot\text{CN}$ with $\text{NH}_2\text{Ph}\cdot\text{HCl}$ at 120° gives phenyldimethylguanidine, m.p. 90° [methiodide, m.p. 188° (decomp.)], but does not react at atm. pressure with $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}_2$ (I) [picrolonate, m.p. 198° (decomp.)]; oxalate, m.p. 171—172°; methiodide, m.p. 222°, $\text{NO}\cdot\text{Bz}_2$ derivative, m.p. 131—132°; piperonylidene derivative, m.p. 105—106°, converted by MeI followed by dil. HCl into $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NHMe}$ (picrolonate, m.p. 196—198°). Piperonaldehyde cyanohydrin is reduced ($\text{Na}-\text{Hg}$) to β -hydroxy- β -3:4-methylenedioxyphenylethylamine [carbonate, m.p. 116—119° (decomp.)]; hydrochloride, m.p. 182—183°; picrolonate, m.p. 200° (decomp.); oxalate, m.p. 197°; $\text{N}\cdot\text{Bz}_1$ derivative, m.p. 152—153°; $\text{NO}\cdot\text{Bz}_2$ derivative, m.p. 141—142°; methiodide, m.p. 229—230°, the piperonylidene derivative, m.p. 155—156°, of which, when methylated and hydrolysed, yields 3:4-methylenedioxyadrenaline (picrolonate, m.p. 203°). (I) condenses with $\text{SMe}\cdot\text{C}(\text{NH})\cdot\text{NH}_2\cdot\text{HI}$ in boiling EtOH, giving β -hydroxy- β -phenylethylguanidine hydriodide, m.p. 133°. A. Li.

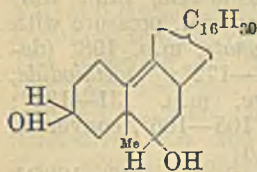
Preparation of a homologue of epicoprosterol in the ergosterol series. F. WETTER and K. DIMROTH (Ber., 1937, 70, [B], 2033).—Further details of the measurements of absorption spectra are given (cf. this vol., 416). H. W.

Bile acids, sterols, neutral saponins, cardiac poisons, hormones, and vitamins and their mutual chemical relationships. D. VAN OS (Pharm. Weekblad, 1937, 74, 1161—1178, 1194—1218).—A review of the chemical relationships of representative members of each of the above types of compounds. S. C.

Stereochemistry of the sterols and the bile acids. D. A. PEAK (Nature, 1937, 140, 280—281).—A discussion. The fusion of the c and d rings appears to be in the *cis* and not in the *trans* position as hitherto believed. L. S. T.

Transformations of cholestanetriol. H. LETTRÉ and M. MÜLLER (Ber., 1937, 70, [B], 1947—1952).—Removal of H_2O from cholestanetriol (I), unlike that from the ergostadienetriols, does not lead to 7-dehydrosterols but is accompanied by stabilisation to the oxide or by intramol. transformations. Distillation at 220—240°/1 mm. of (I) causes decomp. without formation of well-defined substances. The corresponding dibenzoate at 210°/1 mm. gives BzOH and α -cholesteryl oxide benzoate, m.p. 181°. The diacetate is unchanged when distilled but passes when heated with BaCO_3 at 220° into α -cholesteryl oxide acetate, m.p. 97—98°. To exclude the possible formation of an oxide, derivatives of (I) in which OH at C_{15} is removed or replaced are examined. Cholestanetriol diacetate is converted by Ac_2O -conc. H_2SO_4 into a cholestenediol diacetate, hydrolysed to a cholestenediol, m.p. 99—108° (*di*-3:5-dinitrobenzoate, m.p. 231°); the corresponding dibenzoate, m.p. 160—161° and, after solidification, m.p. 177—178°, loses a little BzOH at 210°/1 mm. but is mainly unchanged. Oxidation of the enediol by CrO_3 in AcOH at 4°

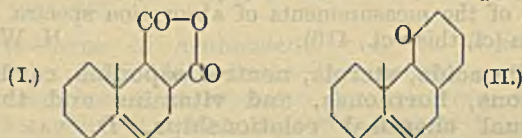
gives a substance (II), $C_{27}H_{42}O_3$ (?), m.p. 142—143°. (I) is transformed by HCl-MeOH into the chlorohydrin, $C_{27}H_{47}O_2Cl$, converted into a diacetate, m.p. 107—108°, and a dibenzoate (III), m.p. 181°, proving that the *tert.* OH at C_{15} in (I) is replaced by Cl. (III) when heated at 210°/1 mm., or with quinoline at 180° loses partly HCl and partly BzOH giving a cholestenediol dibenzoate, m.p. 179°, hydrolysed to a cholestenediol, m.p. 137—138°, oxidised to cholestane-3:6-dione. Assuming that a retro-pinacol transformation has occurred, the annexed formula is suggested for (II). H. W.



Derivatives of 3:17-diols of the cyclopentanopolyphenanthrene series.—See B., 1937, 980.

Unsaturated neutral oxidation products of stigmaterol compounds.—See B., 1937, 980.

Diene synthesis applicable to the sterol group. A. B. MEGGY and R. ROBINSON (Nature, 1937, 140, 282).—1-Methyl-2-vinylcyclohexene, obtained from 2-methylcyclohexenylethyl alcohol by an application of the xanthate reaction, condenses with maleic anhydride in C_6H_6 to form the anhydride (I), m.p. 111.5°. This and the related dibasic acid, m.p. 171°,



gave analytical vals. in agreement with theory. With crotonaldehyde, the diene yields an adduct, $C_{19}H_{24}O_4N_4$ (dinitrophenylhydrazone, m.p. 192°). The 2:4-dinitrophenylhydrazone of the adduct (II) from the diene and cyclohexenone has m.p. 164°. Advantages of the method in relation to the synthesis of cholesterol and analogous substances are discussed. L. S. T.

Preparation of plant growth-promoting substances. I. Ethyl α -naphthylglyoxylate; α -naphthylglycollic acid; α -naphthylacetic acid. F. WILCOXON (Contr. Boyce Thompson Inst., 1937, 8, 467—472).— α - $C_{10}H_7$ - CH_2 - CO_2H is prepared by condensation of $C_{10}H_8$ with Et chloroglyoxylate (47% yield) followed by reduction with HI and red P (90% yield of crude product). Reduction with Na-Hg or with H_2 -Ni gave α -naphthylglycollic acid. A. G. P.

Halogen migrations under the influence of aluminium chloride. IV. C. D. NENITZESOU and J. GAVAT (Ber., 1937, 70, [B], 1883—1886; cf. this vol., 140).—Further examples of migration are recorded. Gradual addition of Δ^1 -cyclohexenyl- or -cyclohexylidene-acetic acid in C_6H_6 to $AlCl_3$ in C_6H_6 gave *p*-phenylcyclohexylacetic acid, b.p. 180°/2 mm., m.p. 112° [Et ester (I), b.p. 168°/5 mm.; corresponding chloride, b.p. 182—183°/14 mm., and amide, m.p. 195.5°], the constitution of which is established by its transformation by MgPhBr into the corresponding carbinol, which is oxidised by CrO_3 in AcOH to *p*-phenylcyclohexanecarboxylic acid. β -cyclo-

Hexylacrylic acid and $AlCl_3$ in C_6H_6 afford β -*p*-phenylcyclohexylpropionic acid (II), b.p. 186—189°/1.5 mm., m.p. 145.5° (Et ester, b.p. 159°/2 mm.). Reduction of (I) by Na and EtOH gives β -*p*-phenylcyclohexylethyl alcohol, b.p. 157°/3.5 mm., m.p. 78°, transformed by red P and I in $CHCl_3$ at room temp. into β -*p*-phenylcyclohexylethyl iodide, b.p. 188°/2 mm. (corresponding bromide, b.p. 171°/6 mm.), whence the nitrile, b.p. 194°/1 mm., and (II). Gradual addition of $AlCl_3$ to cyclohexene, BzCl, and cyclohexane gives Ph cyclohexyl ketone, b.p. 131—134°/5 mm., m.p. 54°, which condenses with Mg and CH_2Br - CO_2Et in C_6H_6 to Et β -hydroxy- β -phenyl- β -cyclohexylpropionate, b.p. 155—158°/5 mm. This is hydrolysed to β -hydroxy- β -phenyl- β -cyclohexylpropionic acid, m.p. 175°, dehydrated by boiling Ac_2O to β -phenyl- β -cyclohexylacrylic acid, b.p. 183°/4 mm., m.p. 144.5°, reduced by Na-Hg to β -phenyl- β -cyclohexylpropionic acid, m.p. 101°. H. W.

Addition of Schiff's bases to methylene-carbonyl compounds. C. LAZZARESCHI (Gazzetta, 1937, 67, 371—373).— $CN\cdot CH_2\cdot CO_2Et$, $CH_2(CO\cdot NH_2)_2$, and $CN\cdot CH_2\cdot CO\cdot NH_2$ resemble $CH_2(CO\cdot)_2$ compounds in combining with $NPh\cdot CHPh$. The respective products are Et β -anilino- α -cyano- β -phenylpropionate, m.p. 140°, β -anilino- β -phenylmethylmalonamide, m.p. 196—197°, and β -anilino- α -cyano- β -phenylpropionamide, m.p. 118—119°. E. W. W.

Homologues of thioprocaine. C. F. LISCHER and C. N. JORDAN (J. Amer. Chem. Soc., 1937, 59, 1623—1624).—NaSH and $CH_2Br\cdot CH_2\cdot NEt_2\cdot HBr$ in abs. EtOH give only bis- β -diethylaminoethyl disulphide, b.p. 160°/16 mm. (dihydrobromide, m.p. 223°). p - $NO_2\cdot C_6H_4\cdot CO\cdot SK$ and $Cl\cdot [CH_2]_3\cdot Br$ in EtOH give γ -chloropropyl *p*-nitrothiobenzoate, m.p. 59—60°, reduced (Fe-HCl) to the *p*-aminothiobenzoate, m.p. 50—51°, which with the appropriate diamine at 100° gives the following γ -dialkylaminopropyl *p*-aminothiobenzoate dihydrochlorides: Et_2 , m.p. 190—191°, Pr^a_2 , m.p. 167°, Pr^a_2 , m.p. 196°, diallyl, m.p. 143°, Bu^a_2 (1:1 compound of the mono- and dihydrochloride), m.p. 162°, and di-*n*-amyl, m.p. 183°. The ester hydrochlorides are local anæsthetics. M.p. are corr. R. S. C.

Dissociation constants of *o*-substituted acids. Alkaline hydrolysis of benzoic esters.—See A., I, 516.

Formation of anilides of acids.—See A., I, 522.

Catalytic hydrogenation of amides of α -hydroxy-acids (cont.). H. ÔEDA (Bull. Chem. Soc. Japan, 1937, 12, 377—381; cf. this vol., 235).—Hydrogenation of $CH_2Ph\cdot CH(OH)\cdot CO\cdot NH_2$ yields $CH_2Ph\cdot CH(OH)\cdot CH_2\cdot OH$ (cf. A., 1936, 189) together with two forms (presumed to be *meso* and *r*) of α -diamino- β - γ -dibenzylbutane, m.p. 153—155° (Bz derivative, m.p. 199—201°) and m.p. 166—167° (Bz, m.p. 280—282°, and $Ph\cdot SO_2$ derivatives, m.p. 226—227°). F. R. G.

Sulphur studies. XII. Thioaldehydes in the naphthalene and anthracene series. J. H. WOOD and R. W. BOST (J. Amer. Chem. Soc., 1937, 59, 1721—1723; cf. this vol., 342).—Naphthalene-(4) and anthracene-thioaldehydes (B) are more

stable than thiobenzaldehydes. The influence of the size of the radical is shown by the fact that PhCHS gives mainly the *trans*-cyclic trimeride, (A) give only the *trans*-cyclic compound, and (B) give only linear polymerides. 1-C₁₀H₇·CHO is best obtained from 1-naphthylcarbithioic acid by way of the semicarbazone. 2:1-OEt·C₁₀H₆·CHO (2:4-dinitrophenylhydrazone, m.p. 258°), best obtained from 2-C₁₀H₇·OMe (I), NPhMe·CHO, and POCl₃, with H₂S and a trace of H₂SO₄ in EtOH gives 2-ethoxynaphthalene-1-thioaldehyde (II), an oil, and some of the cyclic trimeride (III), m.p. 283°, the latter being the sole product if H₂S is passed into a solution of (II) and HCl in EtOH. (II) and 2-C₁₀H₇·CHS are stable in dil. solution for 24–36 hr., give colours with Grote's reagent, eliminate H₂S with 2:4-(NO₂)₂C₆H₃·NH·NH₂ to give the hydrazones, and give ppts. with HgCl₂. At 300°/5 mm. (III) gives 70% of *s-di*-2-ethoxy-1-naphthylethylene, m.p. 213°, but, when distilled with a little H₂SO₄, is partly depolymerised to (II). H₂S and anthracene-9-aldehyde (best obtained from anthracene, NPhMe·CHO, and POCl₃) give a polymeride, m.p. 178°, of anthracene-9-thioaldehyde, obtained faster in presence of HCl; with H₂S and HCl in EtOAc-C₆H₆ at 0° a polymeride, m.p. 266°, is obtained, and at 23° a polymeride, m.p. about 263°; in KOH a polymeride, m.p. 223°, is formed; distillation of these polymerides gives H₂S and tars. R. S. C.

Preparation of vanillin. I–III. S. KIMURA (J. Soc. Chem. Ind. Japan, 1937, 40, 277–278B).—The influence of [KOH], of quantity of KOH and of PhNO₂, and of time, temp., solvents, and catalysts on the oxidation of safrole (I) in the prep. of vanillin (II) is studied. The process (I) → 4:3:1- + 3:4:1-OH·C₆H₃(O·CH₂·OMe)·CH·CHMe → 3:4:1-C₆H₃(OH)₂·CH·CHMe → C₆H₃(OH)₂·CHO → (II) gives improved yields. E. W. W.

3:4-Diphenylchlorocyclopentenones and related compounds. C. F. H. ALLEN and H. RUDOFF (Canad. J. Res., 1937, 15, B, 321–330).—2-Hydroxy-3:4-diphenyl-Δ²-cyclopentenone with POCl₃ affords 2-chloro-3:4-diphenyl-Δ²-cyclopentenone, (I), m.p. 142° (2:4-dinitrophenylhydrazone, m.p. 216–217°), reduced (P-HI-AcOH) to 3:4-diphenylcyclopentanone, m.p. 92° (2:4-dinitrophenylhydrazone, m.p. 228°), which is dehydrogenated (SeO₂ in dioxan) to 3:4-diphenyl-Δ³-cyclopentenone (2:4-dinitrophenylhydrazone, m.p. 233°). Ozonolysis of (I) in EtOAc affords β-benzoyl-β-phenylpropionic acid, and with Na₂CO₃ in MeOH it gives a bimol. compound, C₃₅H₂₈O₃, m.p. 208°. 4-Chloro-3:4-diphenyl-Δ³-cyclopentenone (II) (2:4-dinitrophenylhydrazone, m.p. 216°) with HBr in AcOH yields 2-chloro-3:4-diphenyl-Δ³-cyclopentenone (III) (2:4-dinitrophenylhydrazone, m.p. 216°) and 4:7-endoketo-3:5:6:8-tetraphenyl-4:7:8:9-tetrahydroindenone (cf. A., 1933, 1164), which is also formed from (II) by oxidation (KMnO₄ in COMe₂). 2-Chloro-3:4-diphenyl-Δ³-cyclopentenone (V) with 2:4-(NO₂)₂C₆H₃·NH·NH₂ affords a 2:4-dinitrophenylhydrazone, C₂₃H₁₆O₄N₄, m.p. 265° (decomp.), from which (V) cannot be regenerated. With NaOH-MeOH, (V) yields 4:7-endoketo-2-chloro-3:5:6:8-tetraphenyl-2:3:4:7:8:9-hexahydroindenone, the Cl₁-dimeride, C₃₄H₂₃O₂Cl, of

Burton and Shoppee (A., 1934, 409), from which (IV) is regenerated by NaOMe-MeOH. (IV) with CrO₃ in AcOH affords an isomeride (trans?), m.p. 264°, which at 265–270° yields 3:3:5:6-tetraphenylhydriindone (VI), m.p. 182°, oxidised (SeO₂) to 3:3:5:6-tetraphenylindan-1:2-dione, m.p. 199–200° (monoxime, m.p. about 200°), which with o-C₆H₄(NH₂)₂ gives an anil, m.p. 272°. With HBr-AcOH (VI) affords a dibromide, C₃₃H₂₂OBr₂, m.p. 265°, and with SO₂Cl₂ a dichloride, C₃₃H₂₂OCl₂, m.p. 252°, from which (VI) is regenerated by Zn-AcOH. 1-Phenylcyclohexene and AcCl in CS₂ with SnCl₄ yield 2-acetyl-1-phenyl-Δ¹-cyclohexene, b.p. 145–147°/7 mm. (2:4-dinitrophenylhydrazone, m.p. 165°). The reaction product of CH₂:CMe·CMe:CH₂ and 2:5-diphenylbenzoquinone in MeOH yields on reduction a compound, C₂₂H₂₄O₂, m.p. 169–170°.

J. D. R.

Synthesis of benzantrones. F. G. BADDAR and F. L. WARREN (Nature, 1937, 140, 321; cf. A., 1936, 1388).—The αγ-Et₂ ethers of β-substituted glycerols can be used for the synthesis of 2-alkyl- and 2-aryl-benzantrones under the conditions of Bally and Scholl's synthesis (A., 1911, i, 676). L. S. T.

Infra-red absorption as a measure of enolisation. A. M. BUSWELL, W. H. RODEBUSH, and M. F. ROY (J. Amer. Chem. Soc., 1937, 59, 1767).—The absence of an absorption band characteristic of OH in the region 2·75–3·0 μ. for dibenzoylmethane is believed to indicate that it is not largely in the enolic form (cf. A., 1936, 703). E. S. H.

Carvacrol. VI. Removal of the isopropyl group. VII. Halogenoacylmethylisopropylphenols. I. H. JOHN and P. BEETZ (J. pr. Chem., 1937, [ii], 149, 164–170, 171–174; cf. A., 1936, 76).—VI. AlCl₃ in PhCl (not PhNO₂) at 50° removes the Pr^g from carvacrol, 5-acetyl-, -propionyl-, -n-butyl-, -isovaleryl-, and -benzoyl-carvacrol, thymol, 6-acetyl-, -propionyl-, -n-butyl-, -isovaleryl-, and -benzoyl-thymol to give 53–80% yields of the phenol or OH-ketone. The acyl group is also removed to a small extent. 4-Hydroxy-3-methylpropio-, m.p. 86°, -butyro-, m.p. 133°, and -isovalero-phenone, m.p. 83°, and 4-hydroxy-2-methylbutyro-, m.p. 104°, and -isovalero-phenone, m.p. 51°, b.p. 115–120°/0·008 mm., are described.

VII. Thymol with Br (4 mols.) in CHCl₃ in light gives a Br-derivative, m.p. 113°, and with CH₂Cl·COCl and AlCl₃ in PhNO₂ at 50° gives a 20–23% yield of 6-chloroacetylthymol, m.p. 133°, b.p. 175–178°/0·0018 mm. (acetate, m.p. 83°), sensitive to alkali, with much oily by-product. R. S. C.

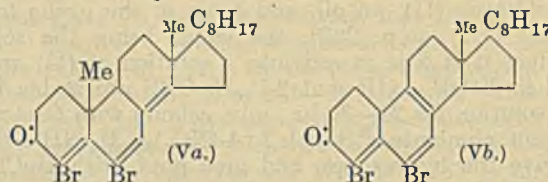
Syntheses in the indene series. H. SIMONIS and G. WOJACK (Ber., 1937, 70, [B], 1837–1848).—Treatment of CHMeBz·CO₂Et with 96% H₂SO₄ at 100° affords 2-methylindandione (I), m.p. 85°, whereas with P₂O₅ 2:2'-dimethylisobindone (II), C₆H₄ < CO > CMe·C < CMe > CO m.p. 198°, is produced, also formed when (I) is warmed with P₂O₅ or boiled with POCl₃. Its constitution is established by its formation from 3-chloro-2-methylindone, m.p. 61° (from CPhCl·CMe·CO₂H and 96% H₂SO₄ at 45–50°), and sodio-2-methylindandione. (II) gives a

p-nitrophenylhydrazone, m.p. 269°, and a *p*-bromophenylhydrazone, m.p. 222° (decomp.), and is converted by *p*-C₆H₄Me·NH₂ and anhyd. ZnCl₂ in boiling EtOH into the *tri-p*-tolil, C₂₀H₁₄(N·C₆H₄Me)₃, decomp. 240—250° after softening at 175°. (II) is transformed by PCl₅ in boiling CCl₄ and subsequently at 160° into the corresponding *dichloride*, m.p. 182°, converted by Cu powder in boiling EtOH into (II) and by HI (*d* 1.7) into *dihydro*-2 : 2'-*dimethylisobindone* (3-2'-methylindandionyl-2-methylindanone), m.p. 154°, also derived from (II), HI (*d* 1.7), and red P in boiling AcOH. 2 : 2'-*Dimethylisobindone dibromide* is obtained from (II) and Br in boiling CS₂ in sunlight. Fuming HNO₃ and (II) in boiling AcOH yield a *dinitrodimethylisobindone*, m.p. 167° (decomp.). Et *o*-toluoylmethylacetate and conc. H₂SO₄ give 2 : 4-*dimethylindan-1 : 3-dione* (III), m.p. 110°. The corresponding *p*-tolyl derivative affords 2 : 6-*dimethylindan-1 : 3-dione*, m.p. 112°, whereas the *m*-tolyl compound yields a *substance*, m.p. 87°. Et α -*m*-xylopropionate is converted into 2 : 4 : 6-*trimethylindan-1 : 3-dione*, m.p. 104°, whereas Et benzoylbenzylacetate with H₂SO₄ or P₂O₅ gives 2-benzoylindanone, m.p. 98°. The formation of methylindandione could not be detected. *o*-C₆H₄Me·CO·CHMe·CO₂Et is converted into 2 : 2' : 4 : 4'-*tetramethylisobindone*, m.p. 129° (*p*-nitrophenylhydrazone, m.p. 218°), also derived from (III), NaOEt-EtOH, and 3-*chloro*-2 : 4-*dimethylindone*, m.p. 107° (obtained from β -*chloro*- α -*o*-*dimethylcinnamic acid*, m.p. 103°). *p*-C₆H₄Me·CO·CHMe·CO₂Et and P₂O₅ at 140° afford 2 : 2' : 6 : 6'-*tetramethylisobindone*, m.p. 193° (*p*-nitrophenylhydrazone, m.p. 251°), obtained also from 3-*chloro*-2 : 6-*dimethylindone*, m.p. 80° [from β -*chloro*- α -methyl-*p*-methylcinnamic acid, m.p. 108° (*Et ester*)], and 2 : 6-*dimethylindandione*. Et α -2 : 4-*dimethylbenzoylpropionate* and P₂O₅ give a cryst. mass which yields 2 : 4 : 6 : 2' : 4' : 6'-*hexamethylisobindone* - *p*-nitrophenylhydrazone, m.p. 232°. Similarly the resinous product from Et α -anisoylpropionate and P₂O₅ affords 6 : 6'-*dimethoxy*-2 : 2'-*dimethylisobindone* - *p*-nitrophenylhydrazone, m.p. 230—235° after softening. 2 : 2'-*Dichloroisobindone* has m.p. 224°.

H. W.

Bromination of Δ^4 -cholesten-3-one, cholestane-3 : 6-dione, and Δ^4 -cholestene-3 : 6-dione. A. BUTENANDT, G. SCHRAMM, and H. KUDBUS (Annalen, 1937, 531, 176—208; cf. A., 1936, 1512).—The bromination of cholestenone is a complex process the final result of which depends greatly on the experimental conditions. A scheme for the probable course of the changes is given. Gradual addition of Br in AcOH to cholestenone (I) in Et₂O containing HBr gives 4 : 6 : 6-tribromo- Δ^4 -cholesten-3-one (II), m.p. 182—183° (decomp.) or m.p. 194° when very rapidly heated, also obtained from the stereoisomeric 4 : 6-dibromo- Δ^4 -cholesten-3-ones. (II) is unchanged by short warming with KOAc or Zn dust in EtOH. 4 : 6-Dibromo- Δ^4 -cholestadien-3-one (III), m.p. 183° (cf. Ruzicka *et al.*, A., 1936, 1382), is obtained by treatment of (I) in CHCl₃ with Br-AcOH at room temp., of (II) in EtOAc by conc. HBr, and from 4 : 4 : 5 : 6-tetrabromocholestanone by KOAc in EtOH-C₆H₆ or by HBr in Et₂O-AcOH at room

temp.; it is unchanged when heated with Ac₂O. Gradual addition of Br in AcOH to (I) in CHCl₃ gives 4 : 6 : 7-tribromo- Δ^4 -cholestadien-3-one (IV), two modifications, m.p. 165—166° and 130° respectively, also obtained by treatment of (III) in Et₂O with Br in AcOH containing conc. HBr. The mother-liquors from the prep. of (IV) by the first method contain *dibromocholestatrienone* (Va or Vb), probably a mixture from which an *individual*, m.p. 203°, [α]_D²⁰ -38° in CHCl₃, is isolated; it is best obtained by



the action of Br in AcOH on (I) in Et₂O and is also derived from (IV), m.p. 165—166°, in CHCl₃ and conc. HBr-AcOH. It is stable towards quinoline at 185° and NPhEt₂ at 215°. It is unaffected by CH₂N₂, maleic anhydride in boiling xylene, Ac₂O, AcCl, AcOH + conc. HCl, Hg(OAc)₂ in EtOH, or by SeO₂ in AcOH or amyl alcohol. The *oxime* has m.p. 118°. (II) with NaI in boiling C₆H₆-EtOH gives 4-bromo-6-ethoxycholestenone (VI), m.p. 111°; if MeOH is used 4-bromo-6-methoxycholestenone, decomp. 101°, is produced. Debromination of (VI) by Zn dust in boiling C₆H₆-MeOH yields (?) 6-ethoxycholestenone, m.p. 109°. Cholestenedione Et ether, m.p. 163°, is produced by the action of HBr-AcOH in boiling EtOH on (IV). Cholestenedione (VII), m.p. 122—123°, is converted by Br in Et₂O-AcOH into 4 : 7-dibromo- Δ^4 -cholestene-3 : 6-dione (VIII), m.p. 174°, which yields a *diquinoxaline* derivative, m.p. 209°; it gives oils containing Br under the influence of AgNO₃ in C₅H₅N. Cholestenedione in CHCl₃ is converted by Br in CHCl₃ containing a little HBr-AcOH into (VIII). (VII) in AcOH with Br at 30—35° affords 4 : 7 : 7-tribromo- Δ^4 -cholestene-3 : 6-dione (IX), m.p. 195°, also obtained from (VIII). Gradual addition of (IX) in C₆H₆ to a boiling mixture of NaHCO₃, Zn dust, and EtOH gives cholestanedione (X) and coprostanedione (XI), similarly derived from (VIII); the respective *dioximes* have m.p. 216° and 143—144°. (XI) is isomerised to (X) in AcOH containing HCl at 100°. Bromination of (XI) in CHCl₃ containing HBr-AcOH gives (VIII). (IX) and AgNO₃ in C₅H₅N at room temp. afford 4 : 7-dibromo- Δ^4 -cholestadiene-3 : 6-dione (XII), m.p. 183°, reduced by Zn dust and AcOH to (X). Cautious treatment of (XII) with Zn dust and boiling EtOH gives 7-bromo- Δ^4 -cholestene-3 : 6-dione, m.p. 216°, transformed by Br in CHCl₃ into (XII). Fe powder and boiling EtOH convert (XII) into 7-bromo- Δ^4 -cholestadiene-3 : 6-dione, m.p. 182°, obtained also from (IX) in boiling C₅H₅N and brominated to (XII).

H. W.

Oxidation of cholesterol and dehydroandrosterone by means of osmic acid. M. USHAKOV and A. LUTENBERG (Nature, 1937, 140, 466).—Oxidation of cholesterol and dehydroandrosterone with OsO₄ yields *cis*-cholestanetriol, and *cis*-androstanonetriol, m.p. 243.5—244° (corr.; sinters at 242.5°), respectively.

L. S. T.

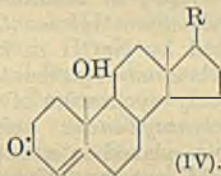
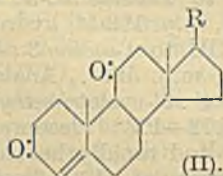
Application of Darzens' reactions to dehydroandrosterone. A. ERCOLI and L. MAMOLI (Chim. e l'Ind., 1937, 19, 435; cf. this vol., 294).—Dehydroandrosterone (I) and $\text{CHCl}_2\cdot\text{CO}_2\text{Et}$ (Mg-Hg) give the *dichloroacetate*, m.p. 198—199°, of (I).

E. W. W.

Sterols. XVIII. Preparation of epiallopregnanolone from allopregnanediol. R. E. MARKER, O. KAMM, and D. M. JONES (J. Amer. Chem. Soc., 1937, 59, 1595—1596).—A good yield of *epiallopregnan-3-ol-20-one* is obtained from *allopregnanediol* by esterifying the 3-OH thereof with $\text{Ac}_2\text{O}\cdot\text{AcOH}$, oxidising the monoacetate with CrO_3 , and separating and purifying the product by means of Girard's reagent and the H succinate. 4-Bromo-20-acetoxypregnan-3-one and $\text{KOAc}\cdot\text{AcOH}$ give 4:20-*diacetoxypregnan-3-one*, m.p. 247°. Hydrogenation (PtO_2 ; 3 atm.) of *pregnanedione*, m.p. 120°, in AcOH gives *isopregnanediol*, m.p. 174° (*diacetate*, m.p. 111°). *alloPregnanonedicarboxylic acid* (from *allopregnanedione* and $\text{CrO}_3\cdot\text{AcOH}$), m.p. 218°, when heated first with Ac_2O and then at 200—280°, and finally distilled at 2 mm., gives *pyroallopregnanedione*, $\text{C}_{20}\text{H}_{30}\text{O}_2$, m.p. 180°.

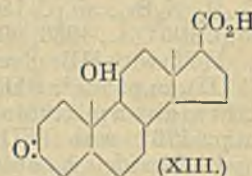
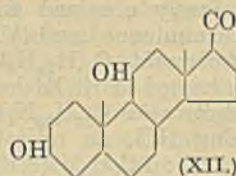
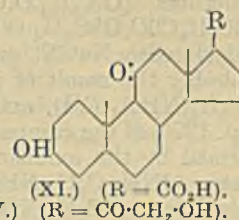
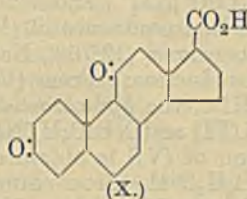
R. S. C.

Adrenal cortex. III. Structures of compounds A, B, and H. H. L. MASON, W. N. HOEHN, B. F. MCKENZIE, and E. C. KENDALL (J. Biol. Chem., 1937, 120, 719—741; cf. this vol., 25).—Compound A (I) (A., 1936, 1117), new formula $\text{C}_{21}\text{H}_{28}\text{O}_4$, is probably (II) ($R = \text{CO}\cdot\text{CH}_2\cdot\text{OH}$). Com-



ound B (III) (*loc. cit.*), new formula $\text{C}_{21}\text{H}_{30}\text{O}_4$, m.p. 177—180° (not 135—139°, cf. *loc. cit.*), $[\alpha]_{\text{D}}^{25} + 222^\circ$ (all rotations in EtOH) (contains 2 OH and 2 CO), is identified with corticosterone (this vol., 105), and is probably (IV) ($R = \text{CO}\cdot\text{CH}_2\cdot\text{OH}$). With HIO_4 , (III) gives CH_2O and acid-2 (V) [formula (IV), $R = \text{CO}_2\text{H}$], new m.p. 253—258° (decomp.), new $[\alpha]_{\text{D}}^{25} + 218^\circ$ (contains 2 active H and 1 CO). Acid-1 (VI) [formula (II), $R = \text{CO}_2\text{H}$], new m.p. 267—269° (*Me ester*, m.p. 178—179°; *mono-oxime*, m.p. 258—260°), from (I) and HIO_4 , is also obtained from (V) and $\text{K}_2\text{Cr}_2\text{O}_7\cdot\text{H}_2\text{SO}_4$ in COMe_2 . Hydrogenation (Pd) of (I) gives *dihydro-compound-A*, $\text{C}_{21}\text{H}_{30}\text{O}_4$ (VII), m.p. 174—176°, $[\alpha]_{\text{D}}^{25} + 163^\circ$, and hydrogenation (Pd) of (III) a *dihydro-compound-B*, $\text{C}_{21}\text{H}_{32}\text{O}_4$ (VIII), [m.p. 181—187°, $[\alpha]_{\text{D}}^{25} + 157^\circ$, further hydrogenated (PtO_2) to *hexahydro-compound-B*, $\text{C}_{21}\text{H}_{36}\text{O}_4$, m.p. 220—222.5°, $[\alpha]_{\text{D}}^{25} + 39^\circ$. Oxidation (HIO_4) of (VIII) gives *dihydro-acid-2* (IX), m.p. 265—270°, $[\alpha]_{\text{D}}^{25} + 100^\circ$ (*Me ester*, m.p. 170—171°). Reduction of (VI) is carried out in steps, and gives first (Pd in EtOH) *acid-1A*, $\text{C}_{20}\text{H}_{28}\text{O}_4$ (X), m.p. 272—273°, $[\alpha]_{\text{D}}^{25} + 114^\circ$ (*mono-oxime*), then (PtO_2 in EtOH-NaOH), *acid-1B*, $\text{C}_{20}\text{H}_{30}\text{O}_4$ (XI), m.p. 272—274°, $[\alpha]_{\text{D}}^{25} + 78^\circ$ (*Me ester*, m.p. 188—189°; no oxime obtained), and, finally ($\text{PtO}_2\cdot\text{AcOH}$) *acid-1C* (XII), $\text{C}_{20}\text{H}_{32}\text{O}_4$, m.p. 284—286°, $[\alpha]_{\text{D}}^{25}$

+71°. Alternatively (X) is obtained by action of $\text{K}_2\text{Cr}_2\text{O}_7\cdot\text{H}_2\text{SO}_4$ on (IX) or on (XI) in COMe_2 . Similar oxidation of (XII) gives *acid-1D* (XIII), $\text{C}_{20}\text{H}_{30}\text{O}_4$, m.p. 265—266°, $[\alpha]_{\text{D}}^{25} + 93^\circ$ (*Me ester*, m.p. 170—171°), but the *acetate* of (XII) with $\text{CrO}_3\cdot\text{AcOH}$ gives the *acetate*, m.p. 210—213°, of (XI). With PCl_5 in CHCl_3 , (XII) gives a *chloro-acid*, $\text{C}_{20}\text{H}_{31}\text{O}_3\text{Cl}$, m.p. 214—217° [*Me ester*, m.p. 128—130°, also obtained by chlorination of the *Me ester* of (XII)]. Filtrates from which (III) has been separated give a gum from which a *compound-H*, $\text{C}_{21}\text{H}_{32}\text{O}_4$ (XIV), m.p. 172—176°, $[\alpha]_{\text{D}}^{25} + 118^\circ$, oxidised (HIO_4) to CH_2O and (XI), and ($\text{K}_2\text{Cr}_2\text{O}_7\cdot\text{H}_2\text{SO}_4\cdot\text{COMe}_2$) to (X) (2:4-dinitrophenylhydrazones), is obtained. The annexed structures are proposed.



As hydrogenation of (I) and (III) largely destroys cortin activity, it is assumed that this is associated with the Δ^4 -unsaturated ketone group.

E. W. W.

Artostenone, a ketonic sterol from *Artocarpus integrifolia*. IV. Oxidation of artostenone. V. Platinichloride of artostenamine. Determination of carbon and hydrogen in stenones. VI. Constitution of artostenone. M. C. NATH (Z. physiol. Chem., 1937, 249, 71—75, 76—78, 78—81; cf. this vol., 294).—IV. Artostenone (I) in COMe_2 with KMnO_4 in neutral or acid (H_2SO_4) aq. COMe_2 gives *diketoartostanic acid*, $\text{C}_{30}\text{H}_{50}\text{O}_4$, m.p. 136° (*dioxime*, m.p. 173°; *anilide* m.p. 140—141°), and with HNO_3 , a *nitrocarboxylic acid*, $\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}$, m.p. 157—159° (decomp.), containing two condensed rings. Artostanone in AcOH with CrO_3 gives a *keto-acid*, $\text{C}_{20}\text{H}_{30}\text{O}_3$ or $\text{C}_{21}\text{H}_{32}\text{O}_3$, m.p. 88—90°.

V. The oxime of (I) in EtOH with Zn and NaOH in EtOH gives *artostenamine*, m.p. 169—170° (*platinichloride*), which with AcOH and NaNO_2 gives *artosterol*. The magnitude of the differences between the C and H contents of such platinichlorides (II) of homologues renders (II) suitable for use in elementary analysis.

VI. (I) in EtOH with H_2SO_4 at 79° for 4 hr. gives α -*artostenone*, m.p. 99—100° (*oxime*, m.p. 193—194°; *CHPh*: compound, m.p. 89—90°). Dihydroartostenone (III) yields a *CHPh*: compound, m.p. 91—92°, but (I) does not. 1 mol. of (I) takes up 2 Br and 1 mol. of (III) 3 Br. (I) is an $\alpha\beta$ -unsaturated ketone with the keto-group at C_{12} and the double linking most probably at $\text{C}_{9}=\text{C}_{11}$.

W. McC.

Unsaturated diketones related to the corpus luteum hormone.—See B., 1937, 980.

Dihydrofollicle hormone.—See B., 1937, 981.

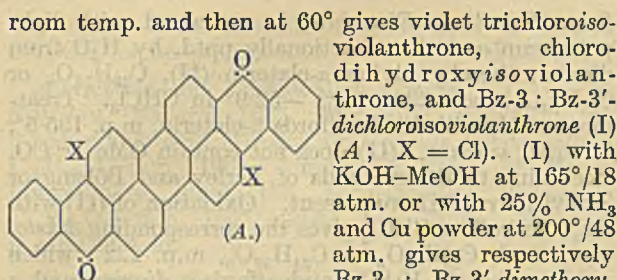
Quinhydrones. R. CIUSA and L. BRULL (Gazzetta, 1937, 67, 392—398).—Quinol (I) treated in EtOH with NaOEt and with benzoquinone (II) gives *disodium quinhydrone* $[\text{O}:\text{C}_6\text{H}_4:\text{O}:\text{O}:\text{C}_6\text{H}_4:\text{O}']\text{Na}_2$, violet, also obtained from quinhydrone and NaOEt, or from (II) and NaOEt. Chloroquinol (III) and chlorobenzoquinone (IV) similarly give *disodium dichloroquinhydrone*. From either (III) and (II), or (I) and (IV), a *disodium chloroquinhydrone* is obtained; it is not clear whether these are identical, or whether they have the different structures $[\text{O}:\text{C}_6\text{H}_4:\text{O}:\text{O}:\text{C}_6\text{H}_3\text{Cl}:\text{O}']\text{Na}_2$ and $[\text{O}:\text{C}_6\text{H}_3\text{Cl}:\text{O}:\text{O}:\text{C}_6\text{H}_4:\text{O}']\text{Na}_2$. Benzoquinoneanil (V) and (I) with NaOEt give a compound (12.76% Na), probably the result of partial reduction. From (V), $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (VI), and aq. HBr, the *hydrobromide*, m.p. 127°, of the compound of (VI) and $\text{NH}:\text{C}_6\text{H}_4:\text{NH}$ [formed by the oxidising action of (V)] is obtained, thus: $[\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{NH}:\text{C}_6\text{H}_4\cdot\text{NH}_2] \cdot \text{Br}$. Similarly (V) and $p\text{-C}_6\text{H}_4(\text{NHPh})_2$ give the *dihydrobromide*, $\text{C}_{36}\text{H}_{32}\text{N}_4\text{Br}_2$, m.p. 180°, previously obtained with m.p. 195° (A., 1936, 991). Benzoquinonedianil (VII) and (VI) with HBr give a *dihydrobromide*, $\text{C}_{24}\text{H}_{24}\text{N}_4\text{Br}_2$ (VIII), m.p. 188°, which when heated in EtOH loses HBr to give a mixture of the *hydrobromide*, $\text{C}_{24}\text{H}_{23}\text{N}_4\text{Br}$, m.p. 173°, with (VIII). Using HCl, an unstable hydrochloride is obtained. 1:2:5- $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2$ and (VII) with HBr or HCl give a *hydrobromide*, $\text{C}_{25}\text{H}_{26}\text{N}_4\text{Br}$, and a *hydrochloride*, m.p. 135°. Similarly $p\text{-C}_6\text{H}_4(\text{NMe}_2)_2$, 2HCl and (VII) give a *green hydrochloride*, m.p. 125° (11.65% Cl). E. W. W.

Colouring matters of *Drosera Whittakeri*.
V. Constitution of droserone. J. W. H. LUGG, A. K. MACBETH, and F. L. WINZOR (J.C.S., 1937, 1597—1600).—The isolation of pure droserone (I) is described, and the measurement of its normal reduction potential supports the proposed structure, 2:5(or 2:8)-dihydroxy-1:4-naphthaquinone, and shows the close relationship to hydroxyjuglone (*diacetate*, m.p. 137°) and phthiocol. The 1:4-naphthaquinone structure of (I) is shown by the absorption spectra of its *acetate*, m.p. 119°. The absorption spectra of phthiocol and naphthapurpurin (*triacetate*, m.p. 164°) are discussed, showing their relationship to lawsone and hydroxydroserone respectively. F. R. S.

Friedel-Crafts reaction. II. Action of phthalic anhydride on acylarylamides. P. KRÄNZLEIN (Ber., 1937, 70, [B], 1952—1963).— $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ and 3:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NHAc}$ react very slowly in CS_2 , Et_2O , or C_6H_6 and slowly in PhNO_2 at 120—140°. In $\text{C}_2\text{H}_2\text{Cl}_4$ at 100—110° $\text{o-2'-acetamido-4':5'-dimethylbenzoylbenzoic acid}$ (I), m.p. 192°, is obtained in 68% yield. Conc. H_2SO_4 at 100° converts (I) into 1-amino-3:4-dimethylantraquinone (II), m.p. 218.5°, with small amounts of $\text{o-2'-acetamido-4':5'-dimethylbenzoylbenzylactam}$ (III), $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2\text{Me}_2$, m.p. 255—256°. Br in boiling AcOH transforms (II) into 2-bromo-1-amino-

3:4-dimethylantraquinone, m.p. 206.5°, which is transformed by CuCl and NaOAc in PhNO_2 at 180—190° into 3:4:3':4'-tetramethylindanthrene; this does not give a vat. Similarly 2-acetamido-5:6:7:8-tetrahydronaphthalene and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ in $\text{C}_2\text{H}_2\text{Cl}_4$ at 70° afford $\text{o-2'-acetamido-4':5'-cyclo-tetramethylenebenzoylbenzoic acid}$ (IV), m.p. 193°, and 5-acetamidohydrindene yields $\text{o-2'-acetamido-4':5'-cyclo-trimethylenebenzoylbenzoic acid}$, (V), m.p. 210°. Attempts to effect ring-closure with (IV) or (V) by H_2SO_4 alone or in presence of H_3BO_3 fail by reason of the more ready sulphonation. Acid chlorides, P_2O_5 , or $\text{AlCl}_3\text{-NaCl}$ are ineffective. Attempts to hydrolyse the NHAc groups by prolonged boiling with dil. HCl lead quantitatively to the *lactams* of (IV) and (V), m.p. 209° and 269°, respectively. The *lactams* are readily hydrolysed by NaOH-MeOH. Thereby (III) yields $\text{o-2'-amino-4':5'-dimethylbenzoylbenzoic acid}$, m.p. 152° (decomp.) and after re-solidification, m.p. 285°; it is transformed into (II). $\text{o-2'-Amino-4':5'-cyclo-tetramethylenebenzoylbenzoic acid}$, m.p. 146.5°, is obtained similarly but its cyclisation is inhibited by sulphonation. Reduction of (IV) by Zn and NH_3 or preferably by H_2 at 170°/40 atm. in neutral or somewhat alkaline solution in a Ni bomb yields $\text{o-2'-acetamido-4':5'-cyclo-tetramethylenebenzoylbenzoic acid}$, m.p. 220°, which with conc. H_2SO_4 at 40—45° gives 1-acetamido-3:4-cyclo-tetramethylenanthrone, m.p. 283° after softening and darkening at 280°; this is oxidised by H_2O_2 in alkaline solution to 1-acetamido-3:4-cyclo-tetramethylenanthraquinone, m.p. 192.5°, hydrolysed by NaOH in boiling MeOH to 1-amino-3:4-cyclo-tetramethylenanthraquinone, m.p. 189°. Analogously cyclisation of $\text{o-2'-amino-4':5'-cyclo-trimethylenebenzoylbenzoic acid}$, m.p. 172—173° (decomp.) when placed in a bath at 165° and rapidly heated, could not be effected. Reduction of (V) affords $\text{o-2'-acetamido-4':5'-cyclo-trimethylenebenzoylbenzoic acid}$, m.p. 238°, whence successively 1-acetamido-3:4-cyclo-trimethylenanthrone, m.p. 277—278° after darkening at 272° and softening at 274°, 1-acetamido-3:4-cyclo-trimethylenanthraquinone, m.p. 212°, and 1-amino-3:4-cyclo-trimethylenanthraquinone, m.p. 212.5°. NHPhAc , *o*-, *m*-, and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NHAc}$, 3:4-, 2:4-, and 2:5- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NHAc}$, and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ do not react with $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$. $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$ is transformed mainly into $\text{o-2'-acetamido-4'-methylbenzoylbenzoic acid}$ (VI), m.p. 184°, transformed by prolonged boiling with dil. HCl into the corresponding *lactam*, m.p. 268°, with a smaller amount of $\text{o-4'-acetamido-2'-methylbenzoylbenzoic acid}$, m.p. 241°, which with conc. H_2SO_4 at 130° affords 2-amino-4-methylantraquinone, m.p. 265°. Similarly (VI) yields 1-amino-3-methylantraquinone, m.p. 193°. H. W.

Regularities of substitution in polynuclear vat dyes. I. Constitution of a dichloro-*isoviolanthrone* and preparation of some *Bz-2:Bz-3'-isoviolanthrone* derivatives. II. Dinitro- and diamino-*isoviolanthrone*s of the *Bz-2:Bz-2'*-series. T. MAKI and Y. NAGAI (Ber., 1937, 70, [B], 1867—1872; 1872—1874).—I. Treatment of *isoviolanthrone* suspended in PhNO_2 with SO_2Cl_2 at



(II) and Bz-3 : Bz-3'-diamino- (III) -isoviolanthrone. The constitution of (I), (II), and (III) follows from the observation that each yields a blue vat which is regarded as characteristic of dibenzanthrone or isodibenzanthrone derivatives disubstituted in the Bz nuclei. Further, oxidation of (I) with $\text{CrO}_3\text{-H}_2\text{SO}_4$ causes almost complete removal of Cl and production of Bz-2 : 3-Bz-2' : 3'-isoviolanthrone-diquinone. Again (I), (II), and (III) dissolves so readily in alkaline $\text{Na}_2\text{S}_2\text{O}_4$ that vat formation takes place at 40—50° whereas isoviolanthrone disubstituted in the *o*- or *m*-position to CO yields vats with greater or less difficulty on account of steric hindrance. The two Cl of (I) are readily replaced by OMe or NH_2 , whereas Cl in β -position of the anthraquinone nucleus reacts with difficulty. 8 : 8'-Dimethoxyisoviolanthrone is a red-violet vat dye whereas (II) gives considerably darker, violet-blue shades on cotton. Bz-2 : Bz-2'-Dimethoxyisoviolanthrone is described.

II (cf. A., 1936, 338). *iso*Violanthrone suspended in AcOH is converted by HNO_3 (*d* 1.48) at 60° into Bz : 2-Bz : 2'-dinitroisoviolanthrone, reduced by $\text{Na}_2\text{S}_2\text{O}_4$ and NaOH to Bz : 2-Bz : 2'-diaminoisoviolanthrone. The greenish-blue shades of the latter on cotton become grey or fast black when the material is treated with NaOCl; warming with NaOH- $\text{Na}_2\text{S}_2\text{O}_4$ on exposure to air reproduces the blue-green colour. The black dye is regarded as Bz : 2-Bz : 2'-isoviolanthrone in which a N_2 group is present either as an intramol. bridge or 2 N_2 groups are distributed between two isoviolanthrone mols.

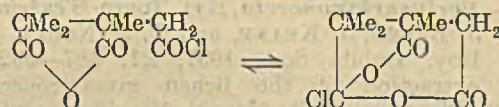
H. W.

Synthetic cyperones and their comparison with α - and β -cyperones. P. S. ADAMSON, F. C. McQUILLIN, R. ROBINSON, and J. L. SIMONSEN (J.C.S., 1937, 1576—1581).—Application of different processes has given cyperones structurally identical with α - and β -cyperones. The respective oximes, semicarbazones, and 2 : 4-dinitrophenylhydrazones of the natural and synthetic ketones exhibit undepressed m.p. on admixture and closely resemble each other in most respects. They show, however, certain optical and crystallographic divergencies, so that complete identity is not claimed. $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and NHET_2 give 1-diethylaminopentan-3-one, b.p. 84°/13 mm., the methiodide of which with *l*-dihydrocarvone and NaNH_2 affords 1-methyl-1- γ -ketoamyl-4-isopropenylcyclohexan-2-one, m.p. 103°. Cyclisation of this compound with NaOEt yields 1 : 10-dimethyl-7-isopropenyl- $\Delta^{1(9)}$ -octal-2-one (I), b.p. 160—163°/11 mm. [α]₅₄₆₁ +88° [oxime (O_a), m.p. 144°; semicarbazone (O_a), m.p. 202°, [α]₅₄₆₁ +91.5° in CHCl_3], and with H_2SO_4 leads to the isomeride, b.p. 130°/1 mm., [α]₅₄₆₁ +342° [oxime (O_β), m.p.

152—153°, [α]₅₄₆₁ +147° in EtOH; semicarbazone (O_β), m.p. 204° (decomp.), [α]₅₄₆₁ +201° in EtOH; 2 : 4-dinitrophenylhydrazone, m.p. 226°]. *l*-Dihydrocarvone, NaNH_2 , and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ give *Et* 1-methyl-4-isopropenylcyclohexan-2-one-1- β -propionate (II), b.p. 181—182°/13 mm., [α]₅₄₆₁ -10.65° in CHCl_3 , which with $\text{Et}_2\text{C}_2\text{O}_4$ followed by loss of CO affords *Et* 3-carbethoxy-1-methyl-4-isopropenylcyclohexan-2-one-1- β -propionate, b.p. 170—175°/3 mm., [α]₅₄₆₁ -29.4° in CHCl_3 (semicarbazone, m.p. 147—148°). This ester is hydrolysed to the acid (semicarbazone, decomp. 192—193°), re-esterified to (II). $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ and (II) yield the β -form of (I), b.p. 173—175°/14 mm., [α]₅₄₆₁ +111.7°, purified through the semicarbazone (B_β), decomp. 209—210° [oxime (B_β), m.p. 141—144°, [α]₅₄₆₁ +112° in EtOH; 2 : 4-dinitrophenylhydrazone, m.p. 225—227°]. Reduction (Na) of this compound gives $\alpha\kappa$ -dimethyl- η -isopropenyldecal- β -ol, b.p. 160°/12 mm. (3 : 5-dinitrobenzoate, m.p. 150—152°), dehydrated to an impure hydrocarbon, b.p. 148°/22 mm., [α]₅₄₆₁ +47.0°.

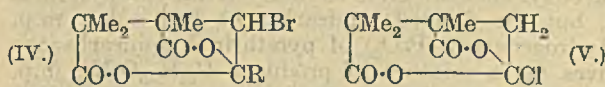
F. R. S.

Desmotropic rearrangements of camphoronic acid derivatives. Constitution of camphoronic and isocamphoronic acids. J. BREDT [with F. DEMEURE (J. pr. Chem., 1937, [ii], 149, 153—163).— α - (I) and β -Camphoronyl chloride (II) with HCO_2H give anhydrocamphoronic acid (III) and with piperidine give a piperidide, m.p. 131.5—132.5°, probably that of (III). Reactions of (I) and (II) and of their Br-derivatives and of camphoronic and isocamphoronic acid, regarded as *cis*- and *cis-trans*-isomerides, $\text{CMe}_2\text{<CO-CO>CH}\cdot\text{CO}_2\text{H}$, are discussed on the basis of desmotropic rearrangement of the chlorides, as annexed.



The following formulæ are assigned: liquid Me_2 camphoronate $\text{CO}_2\text{Me}\cdot\text{CMe}_2\cdot\text{CMe}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$; *Me* α - and β -anhydrocamphoronate $\text{O<CO-CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ and $\text{CO}_2\text{Me}\cdot\text{CMe}_2\text{---CO>O}$, respectively; *Me* camphoronate, m.p. 141—142°, $\text{CO}_2\text{Me}\cdot\text{CMe}_2\cdot\text{CMe}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$;

(III) $\text{O<CO-CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$; bromoanhydrocamphoronic acid, m.p. 154°, $\text{O<CO-CMe}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ and its chloride, m.p. 168° (IV; $\text{R} = \text{Cl}$), and α -*Me* ester, m.p. 100° (IV; $\text{R} = \text{OMe}$), and β -*Me* ester, m.p. 142°, $\text{CO}_2\text{Me}\cdot\text{CMe}_2\cdot\text{CMe}\text{---CO>O}$; α -anhydrocamphoronyl chloride (V).



Bornyl and menthyl *tert*-butylacetates.—See B., 1937, 1134.

Water-soluble ligninsulphonic acid from an extracted oak lignin. H. HIBBERT and W. H. STEEVES (J. Amer. Chem. Soc., 1937, 59, 1768).—Acetylation and hydrolysis of solvent-extracted oak wood meal gives a CHCl_3 -sol. (10%) (OMe 23.6%) and -insol. (90%) lignin (OMe 20.6%), sol. in aq. NaHSO_3 at 100–125°; the sulphonic acid with NaOH gives 4.6% of vanillin and syringaldehyde.

R. S. C.

Lignin. IX. Sulphonation of lignin. H. FRIESE and E. CLOTOWSKI (Ber., 1937, 70, [B], 1986–1989).—The product of the action of H_2SO_4 - Ac_2O - AcOH on Ca ligninsulphonate [obtained by the action of $\text{Ca}(\text{HSO}_3)_2$ on lignin (I)] is the salt, $\text{C}_{36}\text{H}_{41}\text{O}_{20}\text{S}_2\text{Ca}$, closely analogous to the compound, $\text{C}_{36}\text{H}_{39}\text{O}_{21}\text{S}_2\text{Ba}$ (II), derived directly from (I) and H_2SO_4 - Ac_2O - AcOH . A portion of the unsaturated linkings of (I) is unaffected by $\text{Ca}(\text{HSO}_3)_2$ but is sensitive to H_2SO_4 . The presence of an aromatic ring in lignin would be expected to cause a much more energetic action with H_2SO_4 leading to a more highly sulphonated product. $\text{Ca}(\text{HSO}_3)_2$ has no action on (II) at 135°. Nitrolignin is not sulphonated by H_2SO_4 - AcOH - Ac_2O but the presence of a sugar residue becomes evident during the change.

H. W.

Catalytic isomerisation of the acids of pine oleo-resin and rosin. E. E. FLECK and S. PALKIN (J. Amer. Chem. Soc., 1937, 59, 1593–1595).—Isomerisation of *l*-abietic acid (I) by various common catalysts, mostly at 250°, is recorded. Pd-C is the most effective, giving α -pyroabietic acid, $[\alpha]_D^{25}$ about +53°, from (I), α - and β -pimaric and the sapinic acids, and various resins. The reaction is much faster than when heat alone is applied.

R. S. C.

Chemical constituents of lichens found in Ireland—*Pertusaria concreta*, Nyl., form *Westringii*, Nyl. J. BREEN, J. KEANE, and T. J. NOLAN (Sci. Proc. Roy. Dublin Soc., 1937, 21, 587–592).— Et_2O extraction of the lichen gives *concretin*, $\text{C}_{14}\text{H}_7\text{O}_5\text{Cl}_3$, m.p. 287° (decomp.), which contains 3 readily acetylated OH (Ac_3 derivative, m.p. 220–222°) and is methylated with difficulty by CH_2N_2 to a Me_3 derivative, m.p. 200–202°. Extraction of the residue with boiling COMe_2 yields mannitol and norstictic acid, m.p. 267° (decomp.).

P. G. M.

Constituents of pyrethrum flowers. IX. Optical rotation of pyrethrolone and the partial synthesis of pyrethrins. H. L. HALLER and F. B. LAForge (J. Amer. Chem. Soc., 1937, 59, 1678–1681).—Pyrethrolones, obtained from pyrethrins I and II, are identical, being dextrorotatory in both cases. Pyrethrolone and *Me* chrysanthemumcarboxylate-carboxyl chloride, b.p. 88–92°/0.2 mm., yield an oil, which gives no cryst. semicarbazone, but tetrahydropyrethrolone gives tetrahydropyrethrin II, identified as semicarbazone. Chrysanthemumcarboxyl chloride gives similarly tetrahydropyrethrin I, but the derived semicarbazone had a low m.p. Hydrogenation (PtO_2) of pyrethrin I semicarbazone gives (?) a mixture of products, $\text{C}_{22}\text{H}_{35}\text{O}_3\text{N}_3$, m.p. 82–84°.

R. S. C.

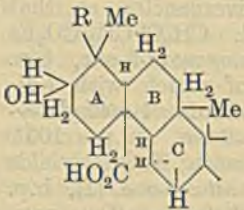
α -Elaterin. L. REICHEL and K. H. EISENLOHR (Annalen, 1937, 531, 287–296).—Elaterin (I) (Merck),

from *Ecballium Elaterium*, is extracted with light petroleum and then fractionally pptd. by H_2O from dioxan, thereby giving α -elaterin (II), $\text{C}_{23}\text{H}_{32}\text{O}_6$ or $\text{C}_{24}\text{H}_{34}\text{O}_6$, m.p. 234°, $[\alpha]_D^{25}$ –52.9° in CHCl_3 . Treatment of (I) with PhMe affords β -elaterin, m.p. 195.5°, in small amount. (II) does not contain OMe or CO . According to the methods of Verley and Bölsing or Zerevitinov 2 OH are present. Oxidation of (II) with Ag_2O in boiling CHCl_3 gives the corresponding *diketo*-compound, $\text{C}_{23}\text{H}_{30}\text{O}_6$ or $\text{C}_{24}\text{H}_{32}\text{O}_6$, m.p. 222°, which reddens fuchsin- H_2SO_3 , and affords a *dioxime* and a *mono-p-nitrophenylhydrazone*. The OH groups are therefore *sec*. Amorphous, ill-defined compounds are obtained from (II) and BzCl , *p*- $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$, diphenylcarbonyl chloride, PCl_5 , or SOCl_2 . Titration of (II) with 0.1N-KOH shows the presence of 1 lactone ring and treatment with 2N-KOH establishes that of 1 Ac, thus accounting for the 6 O. Distillation of (II) with Zn dust gives 1:4- $\text{C}_{10}\text{H}_8\text{Me}_2$, also obtained by use of Se; hence (II) is derived from a hydro-naphthalene. Quaternary Me is absent since dehydrogenation of (II) by S does not give MeSH . With $\text{C}(\text{NO}_2)_4$ (II) gives a distinct yellow colour. Bromination is accompanied by loss of HBr ; it yields amorphous products from which fractions, decomp. 172° and 142°, respectively, have been separated. Hydrogenation (PtO_2 in AcOH) of (II) gives an amorphous H_6 -derivative, transformed by Se at 320° into 1:4- $\text{C}_{10}\text{H}_8\text{Me}_2$ and other substances. Ozonisation of (II) affords AcOH , COMe_2 , and HCO_2H establishing the presence of :CHMe , :CMe_2 , and :CH_2 in the side-chains.

H. W.

Constitution of acid sapogenins. XIII.

Hederagenin and oleanolic acid. Z. KITASATO [with H. SHISHIDO] (Acta Phytochim., 1936, 10, 199–210; cf. A., 1936, 1261).—Oleanonic acid monobromolactone with CrO_3 in $\text{AcOH-H}_2\text{SO}_4$ gave (a) the monobromolactone of oleanintricarboxylic acid, m.p. 270° (decomp.). This is converted by CH_2N_2 into the Me_2 ester, m.p. 190°, which with Zn-AcOH gave Me_2 oleanintricarboxylate, m.p. 203–205°, $[\alpha]_D^{25}$ +57.3° in CHCl_3 . The free acid has m.p. 289–290° (decomp.), and the Me_3 ester, m.p. 167–169°, the latter with KOH-MeOH giving a neutral product, $\text{C}_{28}\text{H}_{44}\text{O}_3$, m.p. 181–183°, $[\alpha]_D^{25}$ +159.4° in CHCl_3 (*oxime*, m.p. 215–216°); (b) the monobromolactone of oleanoltricarboxylic acid which on reduction and methylation as above gave Me_3 oleanoltricarboxylate, m.p. 183°, $[\alpha]_D^{25}$ +73.3° in CHCl_3 . Me_3 keto-oleanintricarboxylate gave a neutral product, $\text{C}_{28}\text{H}_{42}\text{O}_4$, m.p. 178°, $[\alpha]_D^{25}$ +60.9° in CHCl_3 , with KOH-MeOH , and oleanoltricarboxylic acid gave an acid, $\text{C}_{32}\text{H}_{50}\text{O}_6$, m.p. 222–224°. The lactone of Me_2 acetyloleanoldicarboxylate (A., 1936, 1262) is converted by treatment with HBr-AcOH into an isomeric form, m.p. 267–270° (decomp.), which with CH_2N_2 gave a Me_2 ester, m.p. 269–270°, identical with that from the lactone of ketoacetyl-



oleanolic acid by oxidation and methylation. The results fix the structure of the A, B, and C rings as shown, and the structure of the D and E rings is

discussed. Here $R = \text{Me}$ for oleanolic acid and CH_2OH for hederagenin.

P. W. C.

Structure of β -boswellinic acid. J. C. E. SIMPSON (Nature, 1937, 140, 467).—Oxidation of β -boswellinic acid (I) with CrO_3 yields a *monoketone*, $\text{C}_{29}\text{H}_{46}\text{O}$, m.p. 196° . Similar oxidation of Me β -boswellinate gives the corresponding *keto-ester*, $\text{C}_{31}\text{H}_{48}\text{O}_3$, m.p. 160° (*oxime*, m.p. 200°). Thus (I) is a β -OH-acid.

L. S. T.

Structure of gossypol. I. K. N. CAMPBELL, R. C. MORRIS, and R. ADAMS. II. Acylation. R. F. MILLER, D. J. BUTTERBAUGH, and R. ADAMS. III. Gossypol ethers. R. C. MORRIS and R. ADAMS. IV. Anhydrogossypol and its derivatives. R. F. MILLER and R. ADAMS (J. Amer. Chem. Soc., 1937, 59, 1723—1728, 1729—1731, 1731—1735, 1736—1738).—I. Gossypol (I), $\text{C}_{30}\text{H}_{30}\text{O}_8$, exists in *forms*, m.p. 184° (from Et_2O), 199° (from CHCl_3), and 214° (from ligroin), respectively, and in a *red form*, m.p. 184 — 185° (photomicrographs), shown by X-ray examination to be *cryst.*, forms 1:1 *compounds* with AcOH , m.p. 187° , HCO_2H , m.p. 197 — 198° , EtCO_2H , m.p. 177 — 178° , and $\text{Pr}^n\text{CO}_2\text{H}$, m.p. 159 — 160° , and with SnCl_4 gives a *complex* containing 1 Sn and 2 Cl. Its isolation is improved. Colour reactions are described.

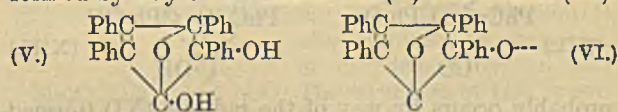
II. The prep. of the white, m.p. 276 — 279° (decomp.; sinters at 265°), and yellow hexa-acetates, m.p. 184 — 186° (decomp.; sinters at 138°), is improved. The former with Ac_2O - NaOAc gives the latter. With conc. H_2SO_4 both or with $\text{Ba}(\text{OMe})_2$ the latter yield (I). Tetra-acetyl-gossypolone is obtained in 57% yield from the white, but only in 7% yield from the yellow, form. Ozonisation of the white form gives a substance, $\text{C}_{19}\text{H}_{20}\text{O}_8$, m.p. 140° . A *hexabenzooate*, m.p. 202 — 204° (decomp.), is obtained.

III. Me_2SO_4 containing 25% of H_2SO_4 converts (I) into a red *Me₆ ether* (II), m.p. 158 — 160° after sintering at 140° , giving in H_2SO_4 an orange colour, hydrogenated to an autoxidisable, colourless H_2 -derivative, which could not be isolated, and unaffected by hot 40% aq. KOH, 30% KOH-EtOH, $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, or $\text{NHPH}\cdot\text{NH}_2$. With Me_2SO_4 in MeOH a colourless *Me₆ ether* (III), *forms*, m.p. 259° (decomp.) and 190° , respectively, is obtained, which gives a scarlet colour with H_2SO_4 , is indifferent to CH_2N_2 , alkali, and FeCl_3 , but is readily oxidised, and gives a Ac_2 derivative, m.p. 264 — 265° [by further acetylation affords a (?) dehydration product, m.p. about 188° after sintering at 140° ; hydrolysed to (III) by KOH-EtOH]. Addition of KOH-MeOH to (I) in Me_2SO_4 gives a mixture of (II) and (III). Addition of Me_2SO_4 to (I) in KOH gives a white *Me₆ ether* (IV), *forms*, m.p. 235 — 237° and 221° , respectively, which gives an orange colour in H_2SO_4 and resembles (II) in properties, but with Ac_2O - NaOAc gives a product, m.p. 179 — 181° after sintering at 160° . Gradual addition of $\text{Na}_2\text{S}_2\text{O}_4$ to (II) in MeOH gives a (?) H_2 -derivative, m.p. 110 — 126° , converted by KOH-MeOH in N_2 into (IV), which regenerates (II) when an excess of 25% NaOH is added to its solution in conc. H_2SO_4 . Addition of 25% NaOH to (I) in Et_2SO_4 - H_2SO_4 gives a *Et₆ ether* (V), m.p. 128 — 130° after sintering at 118° ; addition of KOH-EtOH to (I) in Et_2SO_4 -EtOH gives

a *Et₆ ether*, *forms*, m.p. 211 — 212° and 231 — 232° , respectively.

IV. Anhydrogossypol, $\text{C}_{30}\text{H}_{26}\text{O}_6$, m.p. 230° , best obtained from (I) by $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ in boiling PhMe, probably contains 2 OH (Zerevitinov), with Ac_2O gives a mixture of the two hexa-acetates of (I), regenerates (I) very readily in cold, dil. acids, and affords (II) or (IV) (according to the conditions of methylation) and (V) even in anhyd. media; in liquid NH_3 it gives *diaminogossypol* (VI), $\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_2$, m.p. 228 — 230° after decomp. at 187 — 195° (unstable *hydrochloride*), also obtained similarly from (I) and giving with Ac_2O - NaOAc a $\text{NN}'\text{-Ac}_2$ *tetra-O-acetate*, m.p. 282° (decomp.), and hydrolysed even by warm dil. AcOH to (I). Probably (I) is a symmetrical mol., containing 2 enolic OH; in anhydrogossypol these and two other OH lose 2 H_2O to give $\text{C}\cdot\text{C}\cdot\text{O}\cdot\text{C}$ rings, and (VI) probably contains two $\text{C}\cdot\text{C}\cdot\text{NH}_2$. R. S. C.

Heteropolarity. XXX. Oxidation and reduction products of tetracyclone. R. PÜTTER and W. DILTHEY (J. pr. Chem., 1937, [ii], 149, 183—216; cf. this vol., 425).—Tetracyclone (tetraphenylcyclopentadienone) (I) is converted by various reactions into furan and α -pyrone derivatives. 65% HNO_3 in AcOH or, better, dioxan converts (I) into 2:5-dihydroxy-2:3:4:5-tetraphenylcyclopentenone (II), m.p. 191 — 192° [2 active H (Zerevitinov)]; in AcOH some tetraphenyl- α -pyrone (III), *forms*, m.p. 166 — 167° and double m.p. 158° and 166° , respectively, is also obtained. Dehydration of (II) is effected by hot KOH- $\text{C}_5\text{H}_5\text{N}$ -EtOH, dry HCl - Et_2O , HCO_2H at 100° , or heating at 200° , but yields 2-benzoyl-3:4:5-triphenylfuran (IV), m.p. 166° , which is probably formed by way of the half-acetal (V) and radical (VI).



The structure of (IV) is determined by (a) reduction by distillation with Zn dust or boiling with HI-red P to 2:3:4-triphenyl-5-benzylfuran, m.p. 163° [reconverted into (IV) by amyl nitrite], (b) conversion by MgPhBr into diphenyl-1-2:3:4-triphenylfurylcarbinol, unstable, m.p. 179° (perchlorate, m.p. 267° , a coloured carbenium salt, which with H_2O_2 - AcOH - Ac_2O gives a colourless *hydroperoxide*, m.p. 235 — 238°), (c) Beckmann rearrangement of the *oxime*, m.p. 230° (formed only slowly), by PCl_5 in Et_2O into 2-chloro-3:4:5-triphenylfuran, m.p. 168° (stable to AgOAc), (d) reduction by Zn dust in AcOH to $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-2-3:4:5-triphenylfurylethylene (VII), m.p. 233° (green halochromy in H_2SO_4), and by Al-Hg in KOH-EtOH to 2-3:4:5-triphenylfurylbenzyl alcohol (VIII), m.p. 176 — 177° (red halochromy in H_2SO_4 ; acetate, m.p. 180 — 181°). Br adds as ions to (VII) in CHCl_3 , giving a bluish-green solution, which soon becomes colourless when EtOH is added, owing to formation of the pinacone; disproportionation then gives (IV), but the (VIII) formed could not be isolated. The compound, m.p. 193° , considered by Kohler and Jones (A., 1919, i, 533) to be 2:4-diphenyl-5-benzylfuran, is probably by analogy $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-2-3:5-diphenylfurylethylene. The colourless product (Dilthey *et al.*, A., 1934, 297), intermediate in the form-

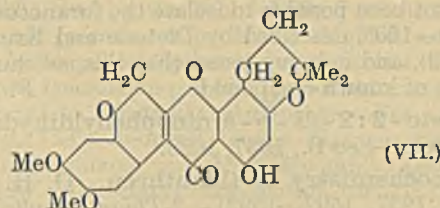
166° (*styril* derivative, m.p. 220°). Alkaline hydrolysis to the corresponding *o*-hydroxybenzoic or naphthoic acid was complete in each case. The mechanism of the reaction is discussed. F. R. G.

Synthesis of rotenone and its derivatives.

XIII. W. BRIDGE, A. J. CROCKER, T. CUBIN, and A. ROBERTSON. **XV.** Structure of toxicarol. S. W. GEORGE and A. ROBERTSON (J.C.S., 1937, 1530—1535, 1535—1542).—**XIII.** 7-Hydroxy-2:2-dimethylchromanone gives no red ferric reaction and forms an acetate, m.p. 91°, *p*-nitrobenzoate, m.p. 137°, and Me ether [2:4-dinitrophenylhydrazone, m.p. 221°; product with semicarbazide acetate, m.p. 226° (decomp.)]. The chromanone is reduced (Clemmensen) to 7-hydroxy-2:2-dimethylchroman (I), m.p. 72° (*p*-nitrobenzoate, m.p. 126°). 7-Hydroxycoumarin (*benzyl ether*, m.p. 154°) is hydrogenated to β-2:4-dihydroxyphenylpropionic acid, converted into 7-hydroxy-3:4-dihydrocoumarin. 7-Benzoyloxy-3:4-dihydrocoumarin and MgMeI yield 7-benzoyloxy-2:2-dimethylchroman, b.p. 160—165°/0.4 mm., debenzylated to (I). 6-Hydroxy-2-isopropylcoumaranone is acetylated to 3:6-diacetoxy-2-isopropylbenzofuran, m.p. 56°, and methylated (MeI) to 6-methoxy-2-isopropyl-β-coumaranone (II), m.p. 78°. Resorcinol Me ether and Et α-bromoisovalerate form α-3-methoxyphenoxyisovaleric acid, b.p. 148—153°/0.1 mm., which is cyclised through the acid chloride to (II). The semicarbazone of 7-methoxychromanone has m.p. 231° (lit. 222°). 7-Benzoyloxy-4-methylcoumarin, m.p. 117.5°, from the OH-compound, with MgMeI gives 7-benzoyloxy-2:2:4-trimethyl-Δ⁸-chromen (III), m.p. 58°, hydrolysed to the 7-OH-compound, m.p. 130°, also obtained through 7-benzoyloxy-2:2-dimethylchromanone, m.p. 73°, and MgMeI. Catalytic reduction of (III) affords 7-hydroxy-2:2:4-trimethylchroman (*p*-nitrobenzoate, m.p. 137°). In forming 2-hydroxy-4-benzoyloxyacetophenone on ozonolysis the behaviour of 7-hydroxy-2:2:4-trimethylchromen is strictly analogous to that of xanthyletin and xanthoxyletin. The foregoing experiments support the structure assigned to 5:7-dihydroxychroman.

XIV. 5:7-Dihydroxy-2:2-dimethylchromanone and MeI-K₂CO₃ give the 5-hydroxy-7-methoxy-compound (IV), m.p. 65—66° (2:4-dinitrophenylhydrazone, m.p. 254°), reduced (Clemmensen) to 5-hydroxy-7-methoxy-2:2-dimethylchroman (V), b.p. 125—128°/0.4 mm. (*p*-nitrobenzoate, m.p. 122°). Benzoylation of (IV) gives 5-hydroxy-7-benzoyloxy-2:2-dimethylchromanone, m.p. 134° (2:4-dinitrophenylhydrazone, m.p. 242°), methylated (MeI-K₂CO₃) to the 7-benzoyloxy-5-methoxy-compound, m.p. 111° (+H₂O, m.p. 81—82°; 2:4-dinitrophenylhydrazone, m.p. 215°), which is debenzylated to the 7-OH-derivative, m.p. 208—209° [2:4-dinitrophenylhydrazone, m.p. 275° (decomp.)]. This substance is also obtained by condensation of phloroglucinol Me ether and ββ-dimethylacryl chloride, and is reduced (Clemmensen) to 7-hydroxy-5-methoxy-2:2-dimethylchroman (VI), m.p. 103—104° (*p*-nitrobenzoate, m.p. 143°). Toxicarol forms an *oxime*, m.p. 236—237°. Dehydrodihydrotoxicarol (VII) with Me₂SO₄-K₂CO₃ gives the Me ether, m.p. 216°, hydrolysed (KOH-Zn) to dihydrotoxicarolic acid Me ether, m.p. 203°, which with hot KOH is converted into derrie

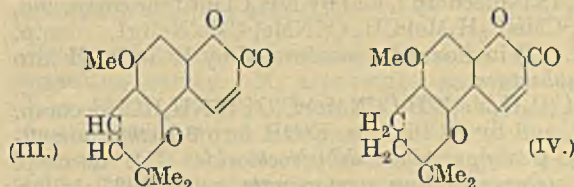
acid and (V) and not (VI). This confirms the structure (VII). 5:7-Dihydroxy-2:2-dimethylchroman



and Me₂-cyanomethyl-4:5-dimethoxyphenoxyacetate after reduction give allodihydrotoxicarolic acid (+H₂O), m.p. 148°, converted (NaOAc-Ac₂O) into the monohydrate of the O-Ac₂ derivative, m.p. 211—212°. Me 2-cyanomethylphenoxyacetate and phloroglucinol afford *phenoxyacetic acid*-2-phloracetophenone, m.p. 184—185°, which with Ac₂O-NaOAc yields the diacetate, m.p. 240—241°, hydrolysed to 5:7-dihydroxychromeno-(3':4':2:3)-chromone, m.p. 256—257°. F. R. S.

Constituents of the bark of *Zanthoxylum americanum* (Mill). **IV.** Constitution of xanthyletin. (Miss) J. C. BELL, W. BRIDGE, and A. ROBERTSON. **V.** Structure of alloxanthoxyletin. A. ROBERTSON and T. S. SUBRAMANIAM (J.C.S., 1937, 1542—1545, 1545—1549).—**IV.** Cresoreylaldehyde, 2:4:5-(OH)₂C₆H₂Me·CHO, m.p. 105—106° (cf. Clemmensen, A., 1914, i, 271), is obtained by reduction of resoreylaldehyde and is itself reduced to *m*-xylorcin. This verifies its orientation and that of 7-hydroxy-6-methylcoumarin (cf. this vol., 72). 7-Hydroxy-2:2-dimethylchroman and HCN-HCl give 7-hydroxy-6-formyl-2:2-dimethylchroman (I), m.p. 104° [2:4-dinitrophenylhydrazone, m.p. 302° (decomp.)], also obtained by ozonolysis of dihydroxanthyletin (II). The structure of (II) is confirmed by its synthesis by decarboxylation of dihydroxanthyletin-3-carboxylic acid, m.p. 158—159°, prepared from (I) and CN·CH₂·CO₂H, followed by hydrolysis. Xanthyletin is reduced (Pd-H₂) to the H₄-compound, m.p. 156°.

V. alloxanthoxyletin (III), C₁₅H₁₄O₄, m.p. 115.5°, has been isolated in small amount from the bark. It is hydrolysed (KOH) to COMe₂ and phloroglucinol Me ether and is reduced (Pd-H₂) to the H₂-compound (IV), m.p. 155°. (IV) is hydrolysed and methylated to *O*-methyl dihydroalloxanthoxyletinic acid, m.p. 178° (decomp.), hydrogenated to the H₁-compound, m.p. 108.5°. Ozonolysis of (IV) affords 7-hydroxy-5-methoxy-8-formyl-2:2-dimethylchroman (V), m.p. 90°, also obtained from 7-hydroxy-5-methoxy-2:2-dimethylchroman and HCl-HCN, and methylated to the



5:7-dimethoxy-compound, m.p. 107°. (IV) may be prepared by decarboxylation of dihydroalloxanthoxyl-

etin-3-carboxylic acid, m.p. 240° (decomp.), obtained from (V) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, followed by hydrolysis. It has not been possible to isolate the furanocoumarin, m.p. 99–100°, described by Dieterle and Kruta (this vol., 112), and it is suggested that this substance is a mixture of known compounds. F. R. S.

1-Keto-2:2-di-p-aminophenyldihydrothionaphthen.—See B., 1937, 1025.

Stereochemistry of thianthren. G. H. KEATS (J.C.S., 1937, 1592–1593).—2-Thianthrenyltrimethylammonium iodide, m.p. 190°, could not be resolved through the *d*-camphor-10- or α -bromo-*d*-camphor- γ -sulphonate or *H d*-diacetyl tartrate. A val. calc. for the energy for transforming thianthren from the folded to the planar state indicates little configurational stability. F. R. S.

2:3-Diketopyrroline, a uninuclear substance related to isatin. O. MUMM and H. HORNHARDT (Ber., 1937, 70, [B], 1930–1947; cf. A., 1911, i, 79).—Hydroxymethylenepinacolindioxime, m.p. 84°, is transformed by AcCl into *tert*-butylisooxazole, b.p. 156°/760 mm., the methosulphate of which is converted by KCN at 0° into α -methylimino- γ -keto- $\delta\delta$ -dimethylhexonitrile, m.p. 42°. This is gradually converted by conc. HCl into $\alpha\gamma$ -diketo- $\delta\delta$ -dimethylhexoic acid (+1H₂O), m.p. 64°, or by less drastic treatment into the corresponding amide, m.p. 115°. The nitrile is transformed by HCl in EtOH into the non-cryst. pyrroline derivative, the constitution of which is established by its scission to γ -imino- α -keto- $\delta\delta$ -dimethylhexoic acid, m.p. 185°, or by aq. EtOH in absence of HCl into $\alpha\gamma$ -diketo- $\delta\delta$ -dimethylhexomethylimide, m.p. 183°. Analogously *Me* hexyl ketone and HCO_2Et with NaOEt give the hydroxymethylene compound, the monoxime, m.p. 118°, of which passes readily into hexylisooxazole, m.p. 97–98°/11 mm. (platinichloride); the corresponding methosulphate is converted by KCN into α -methylimino- γ -ketodeconitrile, which could not be distilled unchanged; when treated with HCl - EtOH it appears to give a pyrroline derivative which could not be isolated, whilst in absence of EtOH it is transformed by aq. dil. or conc. HCl into $\alpha\gamma$ -diketodecoamide, m.p. 99°. $p\text{-C}_6\text{H}_4\text{MeAc}$ gives the corresponding $\text{CH}\cdot\text{OH}$ derivative the oxime, m.p. 133°, of which is converted by AcCl into *p*-tolylisooxazole, m.p. 60°, the methosulphate of which is transformed by KCN into α -methylimino- β -*p*-toluoylpropionitrile (I), m.p. 126°. The constitution of (I) is established by the observation that it yields with MgMeI a product which is decomposed by HCl to the substance

$\text{OH}\cdot\text{CMe}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{C}(\text{NMe})\cdot\text{CMe}\cdot\text{N}\cdot\text{MgI}$, m.p. 175° (decomp.), by AcOH into the compound $\text{OH}\cdot\text{CMe}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{C}(\text{NMe})\cdot\text{CMe}(\text{OH})\cdot\text{NH}\cdot\text{MgI}$, m.p. 183° (decomp.), and by NH_4Cl into the compound, $\text{NH}_2\cdot\text{CMe}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{C}(\text{NMe})\cdot\text{CMe}\cdot\text{N}\cdot\text{MgI}$, m.p. 197°. (I) in dioxan is transformed by HCl - EtOH into the substance

$\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}\cdot\text{C}(\text{NMe})\cdot\text{C}(\text{OEt})\cdot\text{NH}$, HCl , decomp. 145°, and by HCl in abs. EtOH into 3-methylimino-2-keto-5-*p*-tolylpyrroline dihydrochloride (II), decomp. 183° (corresponding monopicrate, m.p. 192°); if a trace of H_2O is present, *Me* α -keto- β -*p*-toluoylpropionate, m.p. 84° [hydrolysed to α -keto- β -*p*-toluoyl-

propionic acid (+1H₂O)], m.p. 143°, is also produced. NaHCO_3 solution and (II) at 0° give the yellow-green ψ -base, $\text{NH}\text{---}\text{C}(\text{C}_6\text{H}_4\text{Me})\text{---}\text{CO}\text{---}\text{C}(\text{OEt})\cdot\text{NH}_2$, which gives *K* (+2H₂O), *Ag* (+1MeOH), decomp. 172°, and *Cu* (+4H₂O), decomp. 191°, salts. NH_3 transforms (II) in EtOH into the compound,

$\text{NH}\text{---}\text{C}(\text{C}_6\text{H}_4\text{Me})\text{---}\text{CO}\text{---}\text{C}(\text{OEt})\cdot\text{NH}_2$, m.p. 153°. Cold H_2O slowly transforms (II) into 2:3-diketo-5-*p*-tolylpyrroline, m.p. 229–230° [*K* (+2H₂O) salt], converted by aq. NaOH into γ -imino- α -keto- γ -*p*-tolylbutyric acid, m.p. 155°. γ -Imino- α -keto- γ -*p*-tolylbutyr-piperidide, m.p. 184°, -amide (+0.5H₂O), m.p. 179°, and -methylamide (+0.5H₂O), m.p. 169°, are formed analogously. The great similarity of (II) to isatin is shown during hydrogenation (PtO_2 in EtOH). Initially a compound resembling isatide is produced which regenerates the parent on contact with air but alternately the air-stable γ -amino- α -hydroxy- γ -*p*-tolyl- Δ^8 -butenoic acid, decomp. 245–250°, results. NH_2Ph and (II) in EtOH afford 3-phenylimino-2-keto-5-*p*-tolylpyrroline (III), m.p. 237°, which under non-standardised conditions yields a mono- and a di-hydrochloride. KOEt and (III) give the *K* salt. Hydrogenation (PtO_2 in EtOH) of (III) affords *Et* γ -amino- α -anilino- γ -*p*-tolylbutyrate, m.p. 123°. $\text{CH}_2(\text{CN})_2$ and (III) in EtOH yield 2-keto-5-*p*-tolyl-3-dicyanomethylenepyrroline, $\text{NH}\text{---}\text{C}(\text{C}_6\text{H}_4\text{Me})\text{---}\text{CO}\text{---}\text{C}(\text{CN})_2$, which has a very high

m.p. It is slowly converted by alkali or piperidine into γ -amino- γ -*p*-tolyl- α -dicyanomethylene- Δ^8 -butenoic acid, m.p. 276°, transformed by boiling HCl - EtOH into the dihydrochloride, m.p. 148–149°, of the substance, $\text{NH}_2\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{C}(\text{NH})\cdot\text{OEt}$. H. W.

dicyclo[1:2:2]Aza-1-heptane. G. R. CLEMO and T. P. METCALFE (J.C.S., 1937, 1523–1526).—*Et* 2:2:5:5-tetramethylpyrrolidine-3-carboxylate-1-acetate, b.p. 169°/16 mm., prepared from $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ and *Et* 2:2:5:5-tetramethylpyrrolidine-3-carboxylate, could not be ring-closed by the Dieckmann reaction. 3-Carboxy-2:2:5:5-tetramethylpyrrolidine-1-acetic acid (+0.5H₂O), m.p. 261°, is obtained by hydrolysis of the ester. 2-Pyrrolidone and $\text{Et}_2\text{C}_2\text{O}_4$ give *Et* 2-pyrrolidone-3-oxalate, m.p. 132°, which could not be ring-closed. Pyridine-4-carboxylic acid, obtained from 2:4-lutidinic acid, is reduced ($\text{Na}\text{---}\text{C}_6\text{H}_{11}\cdot\text{OH}$) and esterified to *Et* piperidine-4-carboxylate, b.p. 74°/1 mm. (picrate, m.p. 172°), which is reduced (Bouveault) to 4-piperidylcarbinol, b.p. 122°/12 mm. (picrate, m.p. 120°). The carbinol with PBr_5 gives the bromide, which in alkaline solution is converted into dicyclo[1:2:2]aza-1-heptane, b.p. 130°/755 mm. [methiodide, m.p. 320° (decomp.); aurichloride, m.p. 280° (decomp.); picrolonate, m.p. 255° (decomp.); picrate, m.p. 274° (decomp.)] (cf. Prelog *et al.*, A., 1936, 1388). F. R. S.

Purification of piperidine and its physiological significance. E. S. COOK and T. H. RIDER (J. Amer. Chem. Soc., 1937, 59, 1739–1741).—The following are recorded for the carefully fractionated materials: piperidine, b.p. 106.3°/751 mm. (hydrochloride, m.p. 248.4–249.9°); 2-methylpiperidine,

b.p. 117—119° (uncorr.)/750 mm. (hydrochloride, m.p. 216—217°); piperidino-, m.p. 172.6—173.6°, and 2-methylpiperidino-formanilide, m.p. 127.9°. M.p. are corr. R. S. C.

Effect of the purification of piperidine on the activity of derived local anæsthetics. T. H. RIDER and E. S. COOK (J. Amer. Chem. Soc., 1937, 59, 1741—1742).—Drugs prepared from pure piperidine often differ in activity from those prepared from material containing 2-methylpiperidine. The following are prepared from the pure bases: piperidino-propanediol diphenylurethane hydrochloride, m.p. 203.5—205°, more active than the crude drug; 2-methylpiperidinopropanediol, m.p. 69—71°, and its *diphenylurethane hydrochloride*, m.p. 192.2—194°; γ -piperidinopropyl benzoate hydrochloride, m.p. 190.6—192.6°; γ -2-methylpiperidinopropyl alcohol, b.p. 110—112°/10 mm., and *phenylurethane*, m.p. 218.5—219°. M.p. are corr. Anæsthetic activities of the urethanes and benzoates are recorded, the Me derivatives being more and less active in the latter and former series, respectively. R. S. C.

Piperidinoacetanilide.—See B., 1937, 1131.

Modification of the Guareschi pyridine synthesis. II. N. PALIT (J. Indian Chem. Soc., 1937, 14, 354—357).—In presence of NaOMe, $\text{CN}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ condenses with Et benzylideneacetate to give the 5-cyano-3-carbethoxy-4-phenyl-6-aryl-2-methylpyridine: *Ph*, m.p. 189° (together with 3:5-dicyano-2:4:6-triphenyldihydropyridine, m.p. 268°), *p*-tolyl, m.p. 189°, *p*-anisyl, m.p. 187°; and with Et benzylidenecyanoacetate to give the 3:5-dicyano-4-phenyl-6-aryl- Δ^3 :6-dihydro-2-pyridone: *Ph*, m.p. 250—251° (NHEt₃ as catalyst gives the diethylammonium salt, m.p. 208—210°), *p*-tolyl, m.p. 293°, *p*-anisyl, m.p. 296°. A. LI.

Manufacture of [pyridinium] methine and polymethine dyes.—See B., 1937, 1032.

Syntheses in the octahydropyrrocoline and octahydropyridocoline series. G. R. CLEMO and T. P. METCALFE (J.C.S., 1937, 1518—1523).—Et piperidyl-1:2-diacetate, b.p. 155°/12 mm., from the monoacetate and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, and K give 2-keto-octahydropyrrocoline (I), b.p. 76—77°/11 mm. [*picrate*, m.p. 187° (decomp.)], which with MgEtI yields 2-hydroxy-2-ethyloctahydropyrrocoline, b.p. 82°/1 mm. (*picrolonate*, m.p. 198°). Dehydration (PCl_5) of the alcohol yields 2-ethylhexahydropyrrocoline (II), b.p. 50°/1 mm. (*picrolonate*, m.p. 191°), catalytically reduced to the H_8 -compound, b.p. 41°/1 mm. [*picrate*, m.p. 149°, *picrolonate*, m.p. 161° (slight decomp.); methiodide, m.p. 232° (decomp.)]. 1-Keto-octahydropyrrocoline (III) and MgEtI give 1-hydroxy-1-ethylhexahydropyrrocoline, b.p. 85—87°/1 mm., dehydrated (PCl_5) to 1-ethylhexahydropyrrocoline, b.p. 74—75°/1 mm. (*picrolonate*, m.p. 185°), which is catalytically reduced to the H_8 -compound (IV), b.p. 64°/11 mm. (*picrate*, m.p. 134°; *picrolonate*, m.p. 176°). Et piperidyl-2-acetate and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ give Et piperidyl-2-acetate-1- β -propionate, b.p. 165—169°/11 mm. Et 1-keto-octahydropyridocoline-2-carboxylate, MeI, and KOEt yield 1-keto-2-methyl-octahydropyridocoline, b.p. 80°/1 mm. (*picrate*, m.p.

176°), which is reduced (Clemmensen) to 2-methyloctahydropyridocoline (V), b.p. 56—57°/1 mm. (*picrate*, m.p. 182°), and by the Wolff method to the isomeric compound (*picrate*, m.p. 158°). MgMeI and (III) yield 1-hydroxy-1-methyloctahydropyrrocoline, b.p. 72—73°/1 mm. (*picrate*, m.p. 142°; *picrolonate*, m.p. 207°), dehydrated to 1-methylhexahydropyrrocoline (*picrolonate*, m.p. 183°), reduced to the H_8 -compound, b.p. 62°/11 mm. [*picrate*, m.p. 191° (decomp.); *picrolonate*, m.p. 198° (decomp.)]. Reduction of (I) by the Wolff and Clemmensen methods gives octahydropyrrocoline, and by the latter method 2-hydroxyoctahydropyrrocoline, b.p. 90°/11 mm. [*picrate*, m.p. 133°; *picrolonate*, m.p. 174° (decomp.)], is also obtained. The isomeric form of the 2-OH-compound, b.p. 95°/14 mm. (*picrate*, m.p. 175°), is obtained by reducing (I) with Na-Hg. Et 2-carbethoxypiperidyl-1- β -propionate and K give Et 1-keto-octahydropyrrocoline-2-carboxylate, b.p. 103°/1 mm. It has now been shown that of the degradation products of strychnine (cf. this vol., 38) the base A is 4-methyl-3-ethylpyridine but B is not (II), (IV), or (V), although it may be another form of (V). F. R. S.

3:3-Di-*p*-aminophenyloxindole.—See B., 1937, 1025.

Condensation of 4-hydroxy-2:6- and -2:8-dimethylquinolines and of their derivatives with aromatic aldehydes. A. MEYER and H. DRUTEL (Compt. rend., 1937, 205, 462—464; cf. A., 1935, 758, 1506; this vol., 389, 431).—The ethiodides of 4-hydroxy-2:6- (I) and -2:8-dimethylquinoline (II) with an excess of aromatic aldehyde and a little piperidine at 130—140° interact at position 2. Thus (I) with the appropriate aldehyde affords: 4-hydroxy-2-(δ -phenyl- Δ^2 -butenyl)-, m.p. 198—199°, -2-(3':4'-methylenedioxy)styryl-, m.p. 271—272°, -2-(4'-methoxy)styryl-, m.p. 260—261°, and -2-(4'-dimethylamino)styryl-6-methylquinoline ethiodide, m.p. 253°. Similarly, (II) affords 4-hydroxy-2-(2'-hydroxy)styryl-, m.p. 248—249°, -2-(4'-hydroxy-3'-methoxy)styryl-, m.p. 210—212°, -2-(3':4'-methylenedioxy)styryl-, m.p. 208—209°, and -2-(4'-dimethylamino)styryl-8-methylquinoline ethiodide, m.p. 218—219°. The OEt-derivative of (II) with $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (III) at 140° in presence of ZnCl_2 affords 4-ethoxy-2-(4'-dimethylamino)styryl-8-methylquinoline, m.p. 174—175°. The reaction is general for the OEt-analogues of (I) and (II). 4-Chloro-2:8-dimethylquinoline with an equimol. amount of (III) in boiling Ac_2O containing some EtOH gives 4-chloro-2-(4'-dimethylamino)styryl-8-methylquinoline, m.p. 127—128°. Similarly treated, (II) or its Bz derivative affords 4-hydroxy-2-(4'-dimethylamino)styryl-8-methylquinoline, m.p. 315—316°, which indicates that acetylation of (II) probably precedes interaction with (III). J. L. D.

Spectrochemical investigations in the isoquinoline series. M. GERENDÁS and E. VARGA (J. pr. Chem., 1937, [ii], 149, 175—182).—Absorption spectra are recorded for piperonyl- (I) and acet- β -hydroxy- β -3:4-methylenedioxyphenylisopropylamide, acet-, piperonyl-, and veratryl- β -hydroxy- β -3:4-dimethoxyphenylisopropylamide, 1-methyl-, 1-piperonyl- (II), and 1-veratryl-3:4-methylenedioxy-

isoquinoline, 1-methyl- and 1-veratryl-3:4-dimethoxyisoquinoline. The amides have a two-banded and the isoquinolines a three-banded spectrum. The intermediate product (A, 1936, 1124) in the synthesis of (II) from (I) is shown by its two-banded absorption spectrum to be *piperonyl- α -piperonylidene-ethylamide*.

R. S. C.

Acridine salts of "yeast" and "muscle" adenylic acids. R. S. TIPSON (J. Biol. Chem., 1937, 120, 621—623).—The acridine salt of "muscle" adenylic acid (I) prepared as described by Wagner-Jauregg has the composition $C_{13}H_9N_2C_{10}H_{14}O_7N_5P$, and not that assigned by him (cf. A., 1936, 743), and m.p. 217—218° (darkening), $[\alpha]_D^{25} -23.2^\circ$ in 10% HCl after 5 min. ($[\alpha]_D^{25}$ calc. for (I), -29.2°). The acridine salt (same formula) of "yeast" adenylic acid (II) has m.p. 183—184° (no previous darkening), $[\alpha]_D^{25} -28.6^\circ$ in 10% HCl after 10 min. ($[\alpha]_D^{25}$ calc. for (II), -35.9°).

E. W. W.

2:8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-groups on the carbon in position 5. XVI. **Synthesis of 5-*m*-aminoanilino-2:8-dialkoxy-10-alkylacridinium derivatives and 5:5'-*m*-phenylenebis(amino-2:8-dialkoxy-*N*-alkylacridinium) derivatives.** K. ISHIHARA (J. Chem. Soc. Japan, 1935, 56, 1368—1387; cf. this vol., 211).—*m*- $C_6H_4(NH_2, HCl)_2$ and 5-chloro-2:8-dimethoxy-10-methylacridinium chloride (I) in H_2O afford 5-*m*-aminoanilino-2:8-dimethoxy-10-methylacridinium chloride hydrochloride (II), $+0.9MeOH$, m.p. 228°, and 5:5'-*m*-phenylenebis(amino-2:8-dimethoxy-10-methylacridinium chloride)*, $+4H_2O$ (III), m.p. 250° (decomp.) (for compounds marked * analysis indicates formation of basic salts), also obtained from (I) and (II). When heated, (II) loses HCl, giving the *acridinium chloride*, which with KOH gives 5-*m*-aminoanilino-2:8-dimethoxy-10-methylacridinium hydroxide (IV), m.p. 110° (decomp.) (with KI in AcOH gives the corresponding iodide, $+0.4AcOH$, m.p. about 225°), also obtained from (III) by KOH. When heated, both the above-mentioned hydroxides dissociate into *m*- $C_6H_4(NH_2)_2$ and 2:8-dimethoxy-*N*-methylacridone. KI in HCl converts (II) into the corresponding *acridinium iodide hydriodide*, $+H_2O$, m.p. 209°, and (III) into the corresponding *bis(acridinium iodide)*, $+0.4AcOH$, m.p. 271° (decomp.). KOH converts (III) into the *bis(acridinium hydroxide)*, m.p. 232°, also obtained from (IV). Similarly are obtained 5-*m*-aminoanilino-2:8-dimethoxy-10-ethyl-, m.p. 173° [corresponding iodide*, m.p. about 220° (*semihydriodide semihydrochloride*, $+1.25H_2O$, m.p. 219°)], -2:8-diethoxy-10-methyl-, m.p. 163° [corresponding iodide*, m.p. 240° (*semihydriodide*, m.p. 237°)], and -2:8-diethoxy-10-ethyl-*acridinium hydroxide*, m.p. 156° [corresponding iodide, $+0.166AcOH$, m.p. 235° (*hydriodide**, $+MeOH$, m.p. 224°)], 5:5'-*m*-phenylenebis(amino-2:8-dimethoxy-10-ethyl-, m.p. 249°, -2:8-diethoxy-10-methyl-, m.p. 193°, and -2:8-diethoxy-10-ethyl-*acridinium hydroxide*), m.p. 193° [corresponding dichlorides, m.p. (* $+3H_2O$) 240° (decomp.), (* $+3H_2O$) 251° (decomp.), and ($+2H_2O, 0.5MeOH$) 259° (decomp.), and *diiodides*, m.p. ($+0.4AcOH$) 271° (decomp.), 253° (decomp.), and 285° (decomp.), respectively]. The original should be consulted.

R. S. C.

1-cycloHexyl-3-methyl-5-pyrazolone.—See B., 1937, 1025.

Synthesis of anserine from *l*-1-methylhistidine. O. K. BEHRENS and V. DU VIGNEAUD (J. Biol. Chem., 1937, 120, 517—522).—*l*-1-Methylhistidine [*l*- α -amino- β -(*N*-methyl-5-glyoxalyl)propionic acid] (I), from anserine (II), and $MeOH-HCl$ give the *dihydrochloride*, m.p. 205°, of the *Me* ester (III) of (I). Carbobenzyloxy- β -alanyl azide (A., 1935, 629) with (III) in $CHCl_3$ gives a syrup converted by NaOH into *carbobenzyloxyanserine*, isolated as the *reineckate*. This is decomposed by C_5H_5N and the product reduced ($Pd-H_2$) to (II), isolated through the Cu salt.

E. W. W.

Creatinine derivatives. III. Alkylation with methyl and ethyl sulphates. Structure of methylcreatinine. W. R. CORNTHWAITE (J. Amer. Chem. Soc., 1937, 59, 1616—1617; cf. A., 1936, 864).—Addition of Me_2SO_4 to creatinine in hot H_2O gives methylcreatinine sulphate, converted by $NaHCO_3$ into methylcreatinine, which yields 5-benzylidene- and furfurylidene-2-methylcreatinine. Et_2SO_4 gives mainly *creatinine Et sulphate*, m.p. 146°, with some ethylcreatinine sulphate. The structure of methylcreatinine is thus confirmed.

R. S. C.

Barbituric acids containing the 2-methylallyl group. W. J. DORAN and H. A. SHONLE (J. Amer. Chem. Soc., 1937, 59, 1625—1626).—The following are prepared: *Et*, n-, b.p. 99°/2 mm., and *iso-propyl*-, b.p. 126—127°/9—10 mm., n-, b.p. 131—132°/3 mm., sec-, b.p. 102—104°/1.5 mm., and *iso-butyl*-, b.p. 110—113°/1 mm., n-, b.p. 112—114°/1 mm., sec-, b.p. 142—144°/8—9 mm., and *iso-amyl*-, b.p. 115—116°/2.5 mm., β -*methyl-n-butyl*-, b.p. 135—137°/7 mm., *n-hexyl*-, b.p. 127—131°/1 mm., β -*ethyl-n-butyl*-, b.p. 129—133°/1 mm., and *allyl- β -methylallylmalonate*, b.p. 124—127°/6 mm.; *Et*, β -*methylallyl*-, b.p. 113—116°/14—17 mm., *di- β -methylallyl*-, b.p. 114—116.5°/1 mm., and *ethyl- α -ethylpropyl-malonate*, b.p. 111—112°/5.5 mm.; 5-*ethyl*-, m.p. 165—167°, -n-, m.p. 173.5—174.5°, and -*iso-propyl*-, m.p. 163—164°, -n-, m.p. 125—126°, -sec-, m.p. 140—142°, and -*iso-butyl*-, m.p. 179.8—180.5°, -n-, m.p. 111—112°, -sec-, m.p. 141.5—143°, and -*iso-amyl*-, m.p. 143.6—144.4°, - β -*methyl-n-butyl*-, m.p. 142—143.5°, - α -*ethylpropyl*-, m.p. 181.5—183°, -*n-hexyl*-, m.p. 127—129°, - β -*ethyl-n-butyl*-, m.p. 148—150°, -*allyl*-, m.p. 165—167°, -*cyclopentyl*-, m.p. 159—161°, -*phenyl*-, m.p. 203—205°, -5- β -*methylallylbarbituric acid*; 5- β -*methylallyl*-, $+0.5H_2O$, m.p. 187—189°, 5:5-*di- β -methylallyl*-, m.p. 207—209°, *N*:5-*diallyl-5- β -methylallyl*-, m.p. 149—150°, and α -*ethylpropyl-barbituric acid*, m.p. 197.5—198°, 5-*n-propyl*-, m.p. 157—158°, -n-, m.p. 137—137.5°, and -*sec-butyl*-, m.p. 138—139°, and -*sec-amyl-5- β -methylallylthiobarbituric acid*, m.p. 146.5—148°. The pharmacological properties of the barbituric acids are summarised.

R. S. C.

Some new derivatives of barbituric acid. M. BUSCH and F. KEYSER (Biochem. Z., 1937, 293, 16—21).—Anilino-barbituric acid, heated with Ac_2O , gave an *acetate*, m.p. 255—260° (decomp.). *Et diethylaminomalonate*, b.p. 98—100°/19 mm., was prepared by heating $NHET_2$ with bromomalonate and when treated with $CO(NH_2)_2$ and $NaOEt$ gave 5-*diethyl*-

aminobarbituric acid, m.p. 350° (decomp.). *Et diisobutylaminomalonate*, b.p. 148—152°/19 mm., was similarly prepared and converted into 5-diisobutylaminobarbituric acid, m.p. 355°. *Et diamylaminomalonate*, b.p. 148—150°/19 mm., with $\text{CO}(\text{NH}_2)_2$ in NaOEt-EtOH gave 5-diamylaminobarbituric acid, m.p. 313°, but when heated in a sealed tube with $\text{CO}(\text{NH}_2)_2$ gave a compound, $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_4$, m.p. 325°. *Et allylaminomalonate*, b.p. 132—135°/19 mm., gave 5-allylaminobarbituric acid, m.p. 232—237°. 5-Bromo-5-ethylbarbituric acid when heated in a sealed tube at 50° with EtOH and NH_4Et gave 5-diethylamino-5-ethylbarbituric acid, m.p. 218—219°. P. W. C.

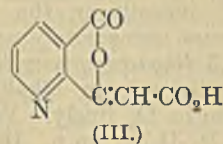
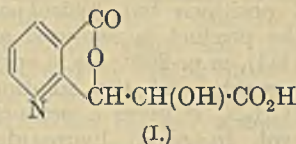
Thiobarbituric acids.—See B., 1937, 1135.

Derivatives of piperazine. X. Reactions with unsaturated esters. II. J. P. BAIN and C. B. POLLARD (J. Amer. Chem. Soc., 1937, 59, 1719—1721; cf. A., 1935, 502).—Piperazine (I) with the appropriate Et_2 arylidenemalonate or aryl aldehyde and $\text{CH}_2(\text{CO}_2\text{Et})_2$ gives 1:4-bis- β -dicarboxy- α -phenyl- (II), m.p. 151—152°, -3:4-methylenedioxyphenyl-, m.p. 150—151°, -o-chlorophenyl-, m.p. 156—157°, -p-anisyl-, m.p. 146—147°, and -2-furyl-ethylpiperazine, m.p. 126—127°. By either method 1-phenylpiperazine gives 1-phenyl-4- β -dicarboxy- α -phenyl-, m.p. 144—145°, -3:4-methylenedioxyphenyl-, m.p. 144—145°, -p-anisyl-, m.p. 146—147°, and -2-furyl-ethylpiperazine, m.p. 130—104°. With hot KOH-EtOH (II) gives (?) K_2 α -ethoxybenzylmalonate and (I). With acid (II) gives (I) and $\text{CHPh}:\text{C}(\text{CO}_2\text{Et})_2$, or PhCHO , $\text{CH}_2(\text{CO}_2\text{Et})_2$, and, in one experiment, $\text{CHPh}:\text{CH}:\text{CO}_2\text{H}$. With H_2 and Raney Ni in dioxan at 100°/68 atm. (II) gives (I), NN' -dibenzylpiperazine, $\text{CH}_2(\text{CO}_2\text{Et})_2$, and $\text{CH}_2\text{Ph}:\text{CH}(\text{CO}_2\text{Et})_2$. The reaction of PhCHO with $\text{CN}:\text{CH}_2:\text{CO}_2\text{Et}$ is catalysed by (I), but no addition occurs. R. S. C.

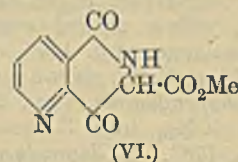
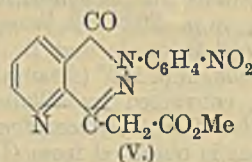
Pyrimidines. I. Preparation of 6-hydroxy-2-methylpyrimidine-5-acetic acid and its derivatives. L. R. CERECEDO and F. D. PICKEL (J. Amer. Chem. Soc., 1937, 59, 1714—1716).— $\text{NH}:\text{CHMe}:\text{NH}_2\cdot\text{HCl}$, $\text{CO}_2\text{Et}:\text{CH}(\text{COH})\cdot\text{CH}_2:\text{CO}_2\text{Et}$, and conc. NaOH give *Et* 6-hydroxy-2-methylpyrimidine-5-acetate (I), m.p. 179—180° (picrate, m.p. 157—158°), the acethydrazide, m.p. 246°, from which with HNO_2 gives 6-hydroxy-2-methyl-5-aminomethylpyrimidine hydrochloride, m.p. 277° (decomp.) (corresponding picrate, m.p. 157—158°), converted by HNO_2 into 6-hydroxy-2-methyl-5-hydroxymethylpyrimidine, m.p. 215°. From (I) are obtained the 5-acetamide, m.p. 242° (picrate, m.p. 207°), and 5-acetic acid, m.p. 254—256°, and with POCl_3 *Et* 6-chloro-2-methylpyrimidine-5-acetate, m.p. 35—36°, b.p. 108—112°/11 mm., which furnishes the phenylhydrazide, m.p. 236°. R. S. C.

Synthesis of 2:5-naphthyridine derivatives. E. OCHIAI, K. MIYAKI, and S. SOTO (Ber., 1937, 70, [B], 2018—2023).— β -2-Carboxyphenylglycerolactone is converted by HCl into isocoumarincarboxylic acid and by H_2O at 250° into isocoumarin; it is therefore a δ -lactone. β -3-Carboxy-2-pyridylglycerolactone (I) on the other hand loses 1 H_2O and 1 CO_2 giving 2-acetylnicotinic acid (II), the constitution of which is confirmed by its oxidation in alkaline solution to CHI_3 and quinolinic acid. It cannot therefore be a

δ -lactone and it appears that it is a γ -lactone (I) which passes into the unsaturated lactone (III) and



thence by ketonic fission into (II). Therefore (I) is transformed through the *Ca* salt into the *Me* ester, m.p. 154°, converted by SOCl_2 in $\text{C}_5\text{H}_5\text{N}$ or by P_2O_5 in boiling xylene into the enol-lactone of *Me* 3-carboxypicolyl-2-acetate (IV) (cf. III), m.p. 160—161°, also formed with a compound, $\text{C}_{10}\text{H}_5\text{O}_4\text{NCl}$, m.p. 108°, by the action of SOCl_2 and $\text{C}_5\text{H}_5\text{N}$ in boiling $\text{C}_6\text{H}_6\text{-PhMe}$. Warm H_2O transforms (IV) into *Me* 3-carboxy-2-picoloylacetate, m.p. 94°, converted by $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}:\text{NH}_2$ into the *p*-nitrophenylhydrazone anhydride (V), m.p. 180°, thus proving that β -3-carb-

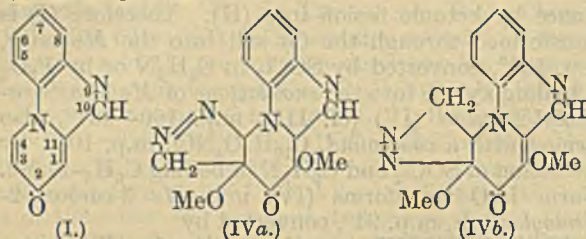


oxy-2-pyridylglyceric acid forms a γ -lactone. CH_2N_2 transforms (IV) into *Me* 3-carbomethoxy-2-picoloylacetate, b.p. 150—155°/0.04 mm., also prepared from the enol-lactone and anhyd. MeOH at 100—110° with small amounts of a compound, m.p. 215°. It gives an oximino-derivative, decomp. 186°, transformed by H_2 (Pd-C in HCl) into *Me* 1:4-dihydroxy-2:5-naphthyridine-3-carboxylate (VI), m.p. 220° (decomp.) after softening at 207°, which with POCl_3 at 120—130° affords *Me* 1-chloro-4-hydroxy-2:5-naphthyridine-3-carboxylate, decomp. 227°. H. W.

Phthaloylation. Action of quinoxaline-2:3-dicarboxylic anhydride on o-phenylenediamine. G. B. CRIPPA and A. AGUZZI (Gazzetta, 1937, 67, 352—358; cf. A., 1929, 706).—Quinoxaline-2:3-dicarboxylic anhydride (I) and $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in EtOH give quinoxaline-3-carboxyl-2'-aminoanilide-2-carboxylic acid (II), m.p. 168°, with $\text{NN}'\text{-o-phenylenebis-}$ (quinoxaline-3-carboxylamide-2-carboxylic acid) (?), m.p. 186—188°. With $o\text{-NHAc}:\text{C}_6\text{H}_4\cdot\text{NH}_2$, (I) gives the *Ac* derivative (III), m.p. 217°, of (II), from which it is also obtained. Either (II) or (III) with Ac_2O in excess gives quinoxaline-2:3-dicarboxyl-2'-acetamidophenylimide, m.p. 310—315°, which with NaOH followed by HCl yields (III). E. W. W.

Derivatives of glucazidone. K. MAURER and B. SCHIEDT [with H. SCHROETER and, in part, H. PLESSING] (Ber., 1937, 70, [B], 1857—1861; cf. A., 1935, 1381).—The typical aromatic reagents attack the pyridone nucleus of glucazidone (I), apparently invariably in position 3. Substitution does not occur with all reagents and if the conditions are made more drastic the ring system is destroyed. Gradual addition of (I) to fuming H_2SO_4 (20% SO_3) gives glucazidone-3-sulphonic acid (II) (+ H_2O), m.p. 275° (decomp.) after darkening (*K*, *Na*, and *Ag* salts). (II) is transformed by fuming HNO_3 into 3-nitroglucazidone, m.p. 215°, also obtained from (I). Oxid-

ation of (II) with aq. KMnO_4 gives quinoxaline-2-carboxylic acid, m.p. 210° . Br appears to substitute (II) initially in the 1:3 positions but hydrolysis occurs immediately and the product is regarded as 1:3-dihydroxyglucazidone (III), m.p. 206° ; it is very readily sol. in alkali hydroxide and the solution absorbs O_2 freely. With CH_2N_2 it gives a product, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_4$, m.p. 186° , sol. in alkali hydroxide,



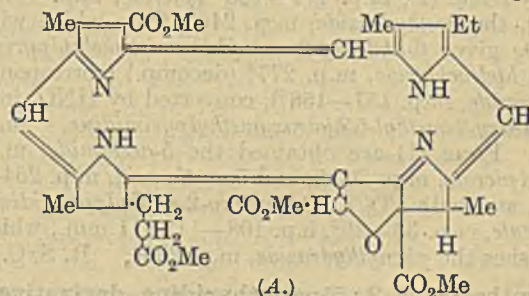
accompanied by a substance (IVa or IVb), m.p. $99-100^\circ$. $\text{NHPh}\cdot\text{NH}_2$ and (IV) afford the *phenylhydrazone*, yellow or red crystals, m.p. 202° . 3-Bromo-glucazidone, m.p. 127° , obtained from (I) and Br in CHCl_3 or C_6H_6 , gives a *methiodide*, m.p. 194° (decomp.) (*methoperchlorate*, m.p. 230°), converted by alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ into 3-bromo-10-keto-9-methylglucazidone, m.p. 178° . 3-Chloroglucazidone is obtained from (II) and SO_2Cl_2 . H. W.

Pyrromethenes and tripyrrylmethanes with bromovinyl groups. H. FISCHER and E. STROBEL (Annalen, 1937, 531, 251—267).—2-Formyl-4-methyl-3-bromovinylpyrrole-5-carboxylic acid (I) condenses readily in MeOH at room temp. with 2:4-dimethylpyrrole (II) to 2-carboxy-3-methyl-4-bromovinyl-di-(2:4-dimethyl)tripyrrylmethane, decomp. 183° . The following 2-carboxy-3-methyl-4-bromovinyl-di-()tripyrrylmethanes are obtained similarly: -2:4-dimethyl-3-ethyl-, -2:4-dimethyl-3- β -carboxyethyl-, decomp. 198° ; -2:3-dimethyl-4-ethyl-, decomp. 158° ; -2:3-dimethyl-, decomp. 169° ; -2-methyl-4-ethyl-, decomp. 141° ; -2:3:4-trimethyl-, decomp. 167° ; -2-methyl-3:4-diethyl-, decomp. 156° ; 2:3-dimethyl-4-propyl-, decomp. 145° ; -3-carbethoxy-2:4-dimethyl-, decomp. 187° ; -2-methyl-3-ethyl-, decomp. 168° . 4-Bromo-2-carboxy-3-methyl-di-(2-methyl-3-ethyl)tripyrrylmethane decomposes at 152° . 2-Carboxy-3-methyl-4-bromovinyl-di-3-benzoyl-2:4-dimethyl- and -3-benzoyl-4-phenyl-2-methyl-tripyrrolmethane and the Et ester of the former could not be thus obtained. Addition of $\text{HBr}\cdot\text{AcOH}$ to (I) and (II) in Ac_2O affords 4:3':5'-trimethyl-3-bromovinylpyrromethene-5-carboxylic acid hydrobromide (Et ester hydrobromide). The requisite pyrrole and (I) (or its Et ester) analogously give the following -3-bromovinylpyrromethene-5-carboxylic acid hydrobromides: 4:4':5'-trimethyl- (Et ester hydrobromide); 4:5'-dimethyl-4'-ethyl- (Et ester hydrobromide); 4:5'-dimethyl-3'-ethyl- (Et ester hydrobromide); 4:3':4':5'-tetramethyl- (Et ester hydrobromide); 4:5'-dimethyl-3':4'-diethyl- (Et ester hydrobromide); 4:4':5'-trimethyl-3'-propyl- (Et ester hydrobromide). 4'-Carbethoxy-4:3':5'-trimethyl-3-bromovinylpyrromethene-5-carboxylic acid hydrobromide and its Et ester hydrobromide, 4'-benzoyl-4:3':5'-trimethyl-3-bromovinylpyrromethene-5-carboxylic acid hydrobromide and its Et ester hydrobromide, and Et 4'-benzoyl-3'-phenyl-4:5'-dimethyl-3-bromovinyl-

pyrromethene-5-carboxylate hydrobromide are described. 3-Bromo-2-formyl-4-methylpyrrole-5-carboxylic acid and 2-methyl-3-ethylpyrrole yield 3-bromo-4:5'-dimethyl-4'-ethylpyrromethene-5-carboxylic acid hydrobromide, converted by Br in AcOH into 3:5-dibromo-4:5'-dimethyl-4'-ethylpyrromethene hydrobromide. 2:4-Dimethyl-3-bromovinylpyrrole-5-carboxylic acid, obtained by hydrolysis of the Et ester, is extremely unstable. 5-Carbethoxy-2-methyl-4-ethylpyrrole-3-acrylic acid suspended in CS_2 is transformed by Br into the corresponding dibromide, which loses HBr at 100° with formation of Et 2-methyl-4-ethyl-3-bromovinylpyrrole-5-carboxylate; this with SO_2Cl_2 in Et_2O yields Et 2-formyl-4-ethyl-3-bromovinylpyrrole-5-carboxylate (oxime), hydrolysed to 2-formyl-4-ethyl-3-bromovinylpyrrole-5-carboxylic acid. Substitution of Et for Me does not appear to increase the stability of these compounds. H. W.

Source of the formic acid produced on acid hydrolysis of nucleic acids. C. D. STEVENS (J. Biol. Chem., 1937, 120, 751—757).—Acid hydrolysis of thymonucleic acid (I) yields HCO_2H (II) corresponding with the adenine (III) present, and adenine sulphate gives on hydrolysis large quantities of (II); from (I), (III), and not the carbohydrate, is therefore presumably the main source of (II), of which guanine (IV) is also a minor source. Yeast nucleic acid on hydrolysis gives (II), due mainly to (III), and partly to (IV) and to ribose. Pyrimidines give little or no (II). E. W. W.

Chlorophyll. LXXX. New purpurins and chlorins by the oxidative degradation of chlorophyll. H. FISCHER and K. KAHR (Annalen, 1937, 531, 209—244).—The presence of CO in purpurin-7 (I) could not be established by NH_2OH or $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, by acetal production or addition of HCl , or by condensation with $\text{CH}_2(\text{CO}_2\text{Et})_2$, $\text{CH}_2(\text{CN})_2$, or MeNO_2 . Benzoylation is not effected in $\text{C}_6\text{H}_5\text{N}$. Chlorin- e_6 , Me_3 ester is oxidised by KMnO_4 in $\text{C}_6\text{H}_5\text{N}$ to dihydroxychlorin- e_6 , and application of this method to purpurin-7 Me_3 ester leads to purpurin-9 [2-carboxy-2-devinylpurpurin-7 Me_4 ester] (A), m.p. 236° (decomp.), which gives a negative

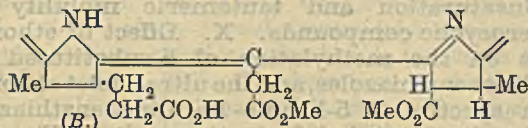


reaction with $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ and is converted by boiling $\text{C}_6\text{H}_5\text{N}$ into 2-carboxy-2-de-ethylrhodoporphyrin Me_3 ester, m.p. 270° . Similar energetic oxidation of isochlorin- e_4 Me_2 ester gives a 2-carboxychlorin sol. in alkali and 5:6-dihydroxy-2-glycolyl-2-devinylisochlorin- e_4 Me_2 ester, m.p. 192° (decomp.). Catalytic hydrogenation (Pd in 1% NaOH) of purpurin-7 Me ester (II) gives meso-rhodochlorin, m.p. 178° , also obtained with meso-purpurin-18 from

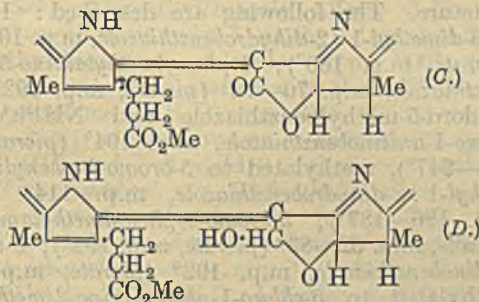
purpurin-18 under similar conditions. With PtO_2 in dioxan *meso*-purpurin-7 Me_3 ester is converted into the *perhydro*-compound, m.p. 213°.

The impossibility of hydrolysing (I) to the tricarbonylic acid depends on the instability in the last stage. Hydrolysis of (II) with $\text{Ba}(\text{OH})_2$ gives the sparingly sol. *Ba* salt of the unstable *chlorin*, $\text{C}_{34}\text{H}_{32}\text{O}_7\text{N}_4\text{Ba}$, $[\alpha]_{\text{D}}^{20} + 650^\circ$ in COMe_2 .

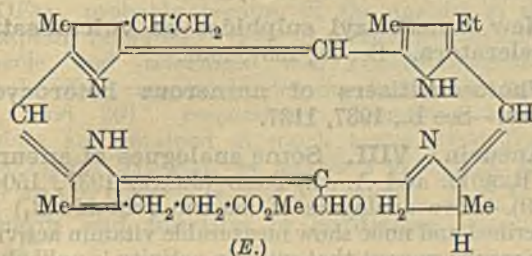
Treatment of phæophorbide *a* (III) in $\text{C}_5\text{H}_5\text{N}$ with MeOH -anhyd. Na_2CO_3 at 100° gives the *chlorin-e}_6* Me_2 ester (*B*), m.p. 215° (decomp.), $[\alpha]_{\text{D}}^{20} - 241^\circ$



in COMe_2 , which when heated above its m.p. yields vinylrhodoporphyrin and a little rhodoporphyrin, both of which are sol. in alkali. (III) is oxidised by KMnO_4 in COMe_2 to unstable *chlorin Me ester*, decomp. 237°, $[\alpha]_{\text{D}}^{20} - 94^\circ$ in COMe_2 . Analogously *meso*-phæophorbide-*a* gives unstable *meso-chlorin Me ester*, m.p. 220° (decomp.), $[\alpha]_{\text{D}}^{20} - 99^\circ$ in COMe_2 . The reactions of these unstable *chlorin* esters do not differ from those of (I). Gentle oxidation of free *chlorin-e}_6* with KMnO_4 appears to give a mixture of *chlorins*, $\text{C}_{33}\text{H}_{34}\text{O}_5\text{N}_4$ and $\text{C}_{32}\text{H}_{34}\text{O}_4\text{N}_4$ or $\text{C}_{32}\text{H}_{32}\text{O}_4\text{N}_4$, esterified by CH_2N_2 to *purpurin-5 Me}_2* ester (IV), m.p. 194°, $[\alpha]_{\text{D}}^{20} + 242^\circ$ in COMe_2 , and the *chlorin ester C* or *D*, m.p. 177°. Free *chlorin-e}_6*



is converted by boiling $\text{C}_5\text{H}_5\text{N}$ in N_2 into *chlorin-e}_4* and another *chlorin*. Under similar conditions but in presence of O_2 it gives the *ester*, $\text{C}_{33}\text{H}_{34}\text{O}_4\text{N}_4$ or $\text{C}_{33}\text{H}_{36}\text{O}_4\text{N}_4$, m.p. 176°. Similarly (IV) gives vinylrhodoporphyrin Me_2 ester, m.p. 273°. Analogously *meso-chlorin-e}_6* affords unchanged material, *meso-chlorin e}_4*, a little porphyrin, and a mixture converted by CH_2N_2 into *meso-purpurin-5 Me}_2* ester, m.p. 127°, $[\alpha]_{\text{D}}^{20} + 79.5^\circ$ in COMe_2 , and the *chlorin Me ester*,



$\text{C}_{33}\text{H}_{36}\text{O}_4\text{N}_4$ or $\text{C}_{33}\text{H}_{38}\text{O}_4\text{N}_4$, m.p. 149°. ψ -*Chlorin-p}_6* yields *diazomethane-meso-chlorinlactone-ester*,

$\text{C}_{33}\text{H}_{34}\text{O}_4\text{N}_4$, m.p. 176°, $[\alpha]_{\text{D}}^{20} - 378^\circ$ in COMe_2 , whilst in the absence of O_2 it affords this substance with *purpurin-5 Me}_2* ester and rhodoporphyrin- γ -carboxylic anhydride. The action of O_2 in $\text{C}_5\text{H}_5\text{N}$ followed by CH_2N_2 on *isochlorin-e}_4* leads to γ -*formylpyrrochlorin Me}_1* ester (*E*), m.p. 181°, $[\alpha]_{\text{D}}^{20} - 401^\circ$ in COMe_2 (*oxime*; *semicarbazone*), also obtained by oxidation with KMnO_4 in $\text{C}_5\text{H}_5\text{N}$. H. W.

Imidomorphyrins. IV. Synthesis of tetraimidomorphyrin. H. FISCHER and F. ENDERMANN (Annalen, 1937, 531, 245—250; cf. this vol., 169).— Et_2 3-methyl-4-ethylpyrrole-2:5-dicarboxylate is converted by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 120—130° into 3-methyl-4-ethylpyrrole-2:5-dicarboxyhydrazide, m.p. 241°, whence the corresponding *diazide*, m.p. 66° (decomp.), which could not be transformed satisfactorily into the corresponding diurethane. Treatment of *opsopyrrole* (I) or *opsoic acid* (II) with Br (2 mols.) does not lead to recognisable derivatives but the simultaneous action of Br and NH_3 in CHCl_3 on (I) gives *tetraimidomorphyrin*, m.p. 252—253° (probably a mixture of isomerides) (corresponding *haemin*, $\text{C}_{38}\text{H}_{32}\text{N}_8\text{FeCl}$, m.p. >380°; complex *Cu* salt, $\text{C}_{28}\text{H}_{32}\text{N}_8\text{Cu}$, m.p. >350°; *Mg* compound, very sensitive to acid). The method can be applied to (II) or 3-methylpyrrole but not to pyrrole itself on account of its ready decomp. by acids. H. W.

Reversible bleaching of chlorophyll. D. PORRET and E. RABINOWITCH (Nature, 1937, 140, 321—322).—In O_2 -free solutions, a reversible bleaching, which \propto the (light intensity)[†], occurs. HCO_2H markedly increases this bleaching, whilst FeCl_2 and traces of O_2 suppress it. The quantum yield of the reversible bleaching is \gg that of the irreversible oxidation in presence of O_2 . Synthetic *Et chlorophyllide a* and the natural chlorophylls *a* and *b* all behave in a similar manner. Possible mechanisms are discussed.

L. S. T.

Reactions of nitrite with haemoglobin derivatives.—See A., III, 411.

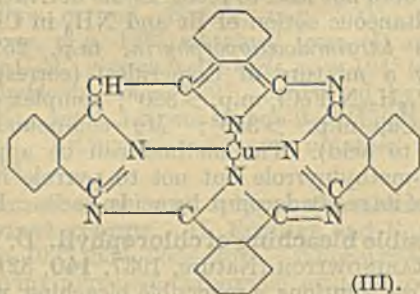
N-Tripyrazolylmethane. W. HÜCKEL and H. BRETSCHNEIDER (Ber., 1937, 70, [B], 2024—2026).—*K* pyrazole, obtained from *K* and pyrazole (I) in C_6H_6 or from molten (I) and KOH , is converted by CHCl_3 in C_6H_6 into *N-tripyrzolylmethane*, m.p. 106°, rapidly transformed by acids into (I) and HCO_2H . BzCl or Bz_2O and (I) afford 1-benzoylpyrazole, b.p. 140°/11 mm., m.p. 46°, also obtained in poor yield from *Mg* pyrazolyl bromide (II) and BzCl . *Me* pyrazole-1-carboxylate, b.p. 92°/11 mm., m.p. 35°, from (I) and ClCO_2Me or from (II), gives CO_2 and (I) when hydrolysed.

Di-1-phenyl-3-methylpyrazolonyl-4-ketone (*semicarbazone*, m.p. 202°) is obtained by the action of H_2O_2 on methenyldi- or methylenedi-phenylmethylpyrazolone. Other attempts to combine three pyrazole residues with one C atom are described. H. W.

Action of cuprous cyanide on o-halogenoacetophenones. II. J. H. HELBERGER and A. VON REBAY (Annalen, 1937, 531, 279—287; cf. this vol., 264).—*o*-Cyanoacetophenone (I), b.p. 148°/12 mm., m.p. 48°, is obtained in very modest yield from *o*- $\text{C}_6\text{H}_4\text{Ac}\cdot\text{NH}_2$ (Sandmeyer); it is prepared from *o*- $\text{C}_6\text{H}_4\text{ClAc}$ and CuCN in quinoline at 160° with a by-

product, m.p. 230°, but is best derived from *o*-C₆H₄BrAc in C₆H₅N at 120° (yield 80%). The unexpected stability of (I) suggests a cyclic structure C₆H₄ < C(NH) > CH₂ or C₆H₄ < C(NH₂) > CH, but the hypothesis is negated by the conversion of (I) by NH₂OH into the inner anhydride of phenylmethylketoxime-*o*-carboxylic acid, C₆H₄ < C(NH) > C(=O)N, m.p. 159°.

Similarly, methylphthalazone, m.p. 219°, is obtained from (I) and N₂H₄·H₂O or NH₂·CO·NH·NH₂. Mild treatment of (I) with NPh·NH₂ in MeOH gives the additive product, C₁₃H₁₅ON₃, m.p. 205–207° (decomp.), converted by short boiling with AcOH into phenylmethylphthalazone. CuCl and (I) in quinoline at 200–220° give the Cu derivative of tetrabenzomonoazaporphin (*loc. cit.*), whilst in presence of *o*-C₆H₄(CN)₂ (II) [(I) : (II) : CuCl :: 2 : 1 : 2] the Cu salt of tetrabenzodiazaporphin results. If the components



are in the ratio 1 : 1 : 1 the product is the Cu derivative of tetrabenzotriazaporphin (III). The intermediate formation of (I) in the production of Cu tetrabenzazaporphins from *o*-halogenoacetophenones and CuCN is thus established.

Exposure of finely-divided *o*-CN·C₆H₄·CH·CH·CO₂H to Br vapour at room temp. gives the corresponding dibromide, m.p. 155°, which passes in boiling C₆H₅N into *ω*-bromo-*o*-cyanostyrene, m.p. 87°, and bromo-*o*-cyanocinnamic acid, m.p. 173°. These compounds with CuCl in quinoline undergo much resinification and do not appear to afford compounds resembling the phthalocyanines (*cf.* Linstead and Noble, this vol., 352).

H. W.

Furfurylbarbituric acids.—See B., 1937, 1135.

Reaction of cysteine with acetone. Titration of cysteine by the acetone-hydrochloric acid method of Linderstrøm-Lang. (Miss) G. E. WOODWARD and E. F. SCHROEDER (J. Amer. Chem. Soc., 1937, 59, 1690–1694).—Cysteine and COMe₂ give H₂O and 2 : 2-dimethylthiazolyldiene-4-carboxylic acid (I), m.p. 134–134.5° (decomp.; corr.), [α]_D²⁵ –183° in COMe₂, hydrolysed by H₂O. In aq. COMe₂ the position of the equilibrium depends on the [COMe₂] and *p*_H. In the Linderstrøm-Lang method of determining glutathione it is essential to add the HCl before the bulk of the COMe₂, as the *p*_H developed prevents the formation of (I), which cannot be titrated with HCl.

R. S. C.

Thiazoles. I. 4-Methylthiazole-5-acetic acid and its derivatives. L. R. CERECEDO and J. G. TOLPIN (J. Amer. Chem. Soc., 1937, 59, 1660–1661).—HCS·NH₂ and Et β-bromolavulate in dry EtOH

at –5° to 15° give Et 4-methylthiazole-5-acetate (I), b.p. 107–112°/3 mm. (hydrochloride, m.p. 153°, prepared slowly from the β-Cl-ester; picrate, m.p. 130°), hydrolysed to the corresponding acid, m.p. 189° {Me ester, b.p. 111°/18 mm.; amide, 136°; hydrazide, m.p. 111° [picrate, m.p. 258° (decomp.)]}. The hydrobromide, m.p. 164°, of (I) with Na–EtOH gives a trace of β-4-methylthiazolyl-5-ethyl alcohol, isolated as picrate, m.p. 164°, but other methods of reduction either did not affect the ester or decomposed it.

R. S. C.

Unsaturation and tautomeric mobility of heterocyclic compounds. X. Effect of ethoxyl ions on the methylation of 5-substituted 1-anilinobenzthiazoles, and the ultra-violet absorption spectra of 5-bromo-1-anilinobenzthiazole and of its *N*-methyl derivatives. R. F. HUNTER and M. A. WALL (J.C.S., 1937, 1513–1517).—On methylation with Me₂SO₄ alone, 1-anilino-5-methyl-, 5-bromo- and 5-chloro-1-anilino-benzthiazole apparently all react exclusively in the amino-aromatic form, yielding 1-phenylimino-2-methyl-1 : 2-dihydrobenzthiazoles. The 5-NO₂-derivative gives a mixture of isomeric Me derivatives. The presence of EtOH–NaOEt causes extensive methylation on the non-nuclear N in the 5-Me-, -Br-, and -Cl-bases, and in the 5-NO₂-compound exclusive alkylation at this position. A comparison of the ultra-violet absorption spectrum of 5-bromo-1-anilinobenzthiazole with that of 5-bromo-1-phenylmethylaminobenzthiazole in EtOH indicates that the mol. has the amino-aromatic structure. The following are described: 1-phenyl-2 : 5-dimethyl-1 : 2-dihydrobenzthiazole, m.p. 107–108° (picrate, m.p. 180°); 1-phenylmethylamino-5-methylbenzthiazole, m.p. 70–72° (picrate, m.p. 192°), from 1-chloro-5-methylbenzthiazole and NPhMe; 5-bromo-1-anilinobenzthiazole, m.p. 194° (picrate, m.p. 246–247°), methylated to 5-bromo-1-phenylimino-2-methyl-1 : 2-dihydrobenzthiazole, m.p. 114° (picrate, m.p. 186–187°); 5-bromo-1-phenylmethylaminobenzthiazole, m.p. 82–83° (picrate, m.p. 198°); 5-chloro-1-anilinobenzthiazole, m.p. 192° (picrate, m.p. 238°), methylated to 5-chloro-1-phenylimino-2-methyl-1 : 2-dihydrobenzthiazole, m.p. 125–126° (picrate, m.p. 174°); 5-chloro-1-phenylmethylaminobenzthiazole, m.p. 76–77° (picrate, m.p. 196–198°); and 5-nitro-1-anilinobenzthiazole, m.p. 248°, methylated to 5-nitro-1-phenylimino-2-methyl-1 : 2-dihydrobenzthiazole, m.p. 210°, and 5-nitro-1-phenylmethylaminobenzthiazole, m.p. 152° (picrate, m.p. 173°).

F. R. S.

5-Chloro-2-(5'-chloro-*o*-toluidino)-3-methylbenzthiazole.—See B., 1937, 1025.

New benzthiazyl sulphides as vulcanisation accelerators.—See B., 1937, 1092.

Photosensitisers of numerous heterocyclic types.—See B., 1937, 1137.

Aneurin. VIII. Some analogues of aneurin. F. BERGEL and A. R. TODD (J.C.S., 1937, 1504–1509).—Five analogues of aneurin (vitamin-B₁) are described and none show measurable vitamin activity. The results suggest that vitamin activity is unlikely in a 3-(pyrimidyl-5'-methyl)thiazolium salt unless it contains (a) a 4'-NH₂, (b) a 5-β-hydroxyethyl group,

(c) a free 2-position in the thiazole ring. It is also probable that the nature of the substituents at 2' and 6' in the pyrimidine ring influences vitamin activity. 4-Amino-5-thioformamidomethyl-2-methylpyrimidine and $\text{CH}_2\text{Cl}\cdot\text{COMe}$ give 3-(4'-amino-2'-methylpyrimidyl-5'-methyl)-4-methylthiazolium chloride hydrochloride (analogue A) ($+\text{H}_2\text{O}$), sinters $261\text{--}262^\circ$. 4-Hydroxy-5-thioformamidomethyl-2-methylpyrimidine (I) and Me α -bromo- γ -acetoxypropyl ketone (II) afford 3-(4'-hydroxy-2'-methylpyrimidyl-5'-methyl)-4-methyl-5- β -hydroxyethylthiazolium chloride hydrochloride (analogue B), m.p. $195\text{--}197^\circ$. $\text{CH}_2\text{Cl}\cdot\text{COMe}$ and (I) yield 3-(4'-hydroxy-2'-methylpyrimidyl-5'-methyl)-4-methylthiazolium chloride hydrochloride (analogue C), ($+\text{H}_2\text{O}$), softens 220° . Condensation in AcOH at 120° of (II) and 4-amino-5-thioacetamidomethyl-2-methylpyrimidine (III), m.p. $228\text{--}229^\circ$, obtained from 4-amino-2-methylpyrimidine and dithioacetic acid, gives the hydrobromide of 2:7-dimethyldihydro-1:3:6:8-benzotetrazine, m.p. $283\text{--}284^\circ$ (picrate, m.p. $198\text{--}199^\circ$; hydrochloride, m.p. $269\text{--}270^\circ$; base, m.p. $169\text{--}170^\circ$), and the bromide hydrobromide of O-acetyl-2-methylaneurin, m.p. $193\text{--}194^\circ$. This compound is converted through the picrate, m.p. $188\text{--}189^\circ$, into 3-(4'-amino-2'-methylpyrimidyl-5'-methyl)-2:4-dimethyl-5- β -hydroxyethylthiazolium chloride hydrochloride (methylaneurin), m.p. 199° . (II) and (III) in AcOH at 80° lead to the hydrobromide of (III), m.p. $198\text{--}200^\circ$, converted through the picrate into the corresponding hydrochloride, m.p. $197\text{--}199^\circ$. 2:4-Dichloro-6-methyl-5-chloromethylpyrimidine (IV) and 4-methyl-5- β -hydroxyethylthiazole afford 3-(2':4'-dichloro-6'-methylpyrimidyl-5'-methyl)-4-methyl-5- β -hydroxyethylthiazolium chloride, m.p. 206° (cf. Bowman, this vol., 213), aminated to the 3-(2'-chloro-4'-amino-compound ($+\text{H}_2\text{O}$), m.p. $200\text{--}205^\circ$ (picrate, m.p. $214\text{--}215^\circ$), which shows no measurable vitamin activity. (IV) and NaI yield 2:4-dichloro-6-methyl-5-iodomethylpyrimidine, m.p. $93.5\text{--}94.5^\circ$, which with 4-methyl-5- β -hydroxyethylthiazole forms 3-(2':4'-dichloro-6'-methylpyrimidyl-5'-methyl)-4-methyl-5- β -hydroxyethylthiazolium iodide, m.p. $181\text{--}182^\circ$. Amination of (IV) leads to bis-(2:4-dichloro-6-methylpyrimidyl-5-methyl)amine, m.p. $162\text{--}163^\circ$, and no 5-aminomethyl compound can be isolated. F. R. S.

Anthraquinonebis-selenazoles.—See B., 1937, 1030.

Improved cyanine synthesis (mixed solvent process). Reaction of orthothioformic ester. T. KIMURA (Proc. Imp. Acad. Tokyo, 1937, 33, 261—265).— $\text{CH}(\text{SEt})_3$ in Ac_2O at 140° gives much better yields of trinuclear carbocyanines than does $\text{CH}(\text{OEt})_3$, probably because of the acidity of the mercaptan liberated; thus, 1-methylbenz-oxazole, -thiazole, and -selenazole, and 1-methyl-naphtho-thiazole afford compounds, decomp. 225° , $260\text{--}261^\circ$, 239° , and 201° , respectively. Dinuclear carbocyanines are obtained in much better yield from $\text{CH}(\text{SEt})_3$ or $\text{CH}(\text{OEt})_3$ by mixtures of $\text{C}_6\text{H}_5\text{N}$ and Ac_2O than by either $\text{C}_6\text{H}_5\text{N}$ or Ac_2O alone. R. S. C.

Origin and function of hordenine.—See A., III, 447.

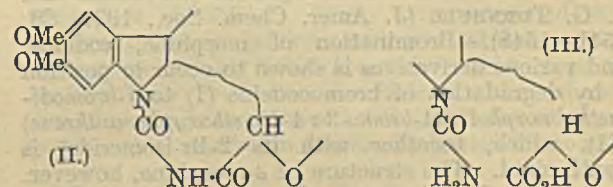
Condensation of 2-aminonicotine with α -bromoacetophenone. J. L. GOLDFARB and M. V.

ANDRIJTSCHUK (Compt. rend. Acad. Sci. U.R.S.S., 1937, 16, 473—477).—2-Aminonicotine and $\text{COPh}\cdot\text{CH}_2\text{Br}$ in EtOH yield a mixture of 7-(N-methylpyrrolidyl)-2-phenylpyriminazole (picrate, m.p. $209.5\text{--}211^\circ$; dihydrobromide, m.p. $272\text{--}274^\circ$; platini-chloride, m.p. $250\text{--}253^\circ$) and α -phenacylaminonicotine (picrate, m.p. 186.5°). J. D. R.

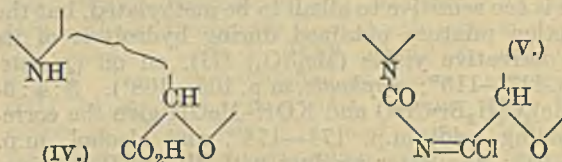
Veratrine alkaloids. II. Basic degradation products of cevine. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1937, 120, 447—456; cf. this vol., 355).—The base $\text{C}_7\text{H}_{15}\text{N}$ has been identified as *d*-N-methyl- β -pipecoline (picrate of *l*-base, m.p. $176\text{--}179^\circ$, $[\alpha]_{\text{D}}^{25} -12.6^\circ$ in COMe_2 ; picrate of *dl*-base, m.p. $165\text{--}168^\circ$). 1-N-Dimethyl- β -pipecolinium iodide, m.p. $200\text{--}201^\circ$, $[\alpha]_{\text{D}}^{25} +7.0^\circ$ in H_2O , and *l*- β -pipecoline 3:5-dinitrobenzoate, m.p. $114\text{--}116^\circ$, $[\alpha]_{\text{D}}^{25} -30^\circ$ in COMe_2 , are described. Separation of the mixture of bases obtained by heating cevine (I) in H_2 with Zn dust, by means of HNO_2 , gave β -pipecoline (II) and similar treatment of the bases obtained by heating with soda-lime gave (II), mainly as the *d*-isomeride, and a very small amount of conine (3:5-dinitrobenzoate, $[\alpha]_{\text{D}}^{25} +49^\circ$ in COMe_2). The base $\text{C}_8\text{H}_{11}\text{N}$ obtained by heating (I) in H_2 with Zn, followed by catalytic hydrogenation, is probably 5-methyl-2-ethylpyridine. The dicyclic base $\text{C}_{10}\text{H}_{19}\text{N}$ previously obtained may be a methyloctahydro-pyridocoline or a dimethyloctahydropyrococline.

J. N. A.

Strychnos alkaloids. XIX. Attempted degradation of oximinobrucine. H. WIELAND and F. WILLE (Annalen, 1937, 531, 268—278; cf. A., 1932, 629).—Oximinobrucine is converted by SOCl_2 into a product (I) from which by repeated crystallisation from MeOH the cyclic carbamide (II), m.p.

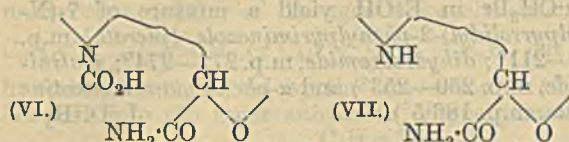


228° (decomp.), is isolated as the hydrochloride, $[\alpha]_{\text{D}}^{25} +30.1^\circ$ in H_2O . Boiling $2\text{N}\cdot\text{H}_2\text{SO}_4$ converts (II) into the open carbamide (III), m.p. 251° (decomp.), $[\alpha]_{\text{D}}^{25} +31.2^\circ$ in $0.1\text{N}\cdot\text{NaOH}$ (sulphate), reconverted into (II) by HCl in MeOH. Treatment with boiling



conc. NaOH transforms (III) into norbrucic acid, $\text{C}_{22}\text{H}_{26}\text{O}_5\text{N}_2$, (IV), m.p. $292\text{--}293^\circ$ (decomp.) (also $+5\text{H}_2\text{O}$) (hydrochloride; Et ester, m.p. 231°), hydrogenated (PtO_2 in AcOH) to dihydronorbrucic acid, m.p. $286\text{--}287^\circ$ after decomp. from 270° (also $+3\text{H}_2\text{O}$). The isolation of an isomeric acid, m.p. 259° (decomp.) after softening, is also described; unlike (IV), it is not hydrogenated in presence of Pd. If (I) is treated with $\text{N}\cdot\text{NaOH}$ (II) present therein is converted into

(III) which dissolves leaving the cyclic *chloroimine* (V), $C_{23}H_{24}O_4N_3Cl$, m.p. 247° (decomp.), converted



by $2N-H_2SO_4$ into (IV), which absorbs $1 H_2$ (Pd-black) without loss of Cl. When finely dispersed (V) is transformed by $2N-NaOH$ into the *carbamic acid* (VI), $C_{23}H_{27}O_6N_3$, m.p. $206-207^\circ$ (decomp.), which with dil. acid yields CO_2 and *norbrucamide* (VII), $C_{22}H_{27}O_4N_3$, m.p. $156-158^\circ$. If a solution of (VII) in dil. HCl is neutralised with $NaHCO_3$ (VI) is obtained. Attempts to remove Cl from (V) by $KOH-EtOH$ yield a *base*, $C_{23}H_{25}O_6N_3$, m.p. $143-145^\circ$, isomeric with (II). The *bases*, $C_{22}H_{25}O_4N_3$, m.p. 258° (decomp.), and $C_{21}H_{26}O_6N_3$, m.p. 163° after prolonged softening [orange-yellow *hydrochloride*; H_4 -derivative, m.p. 236° (decomp.)], are isolated as by-products of the prep. of (I).

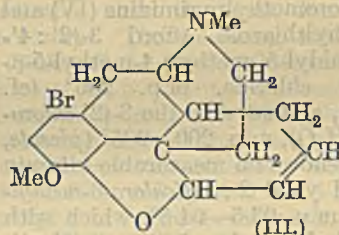
[With H. BEYER.] Re-examination of the acid from 11-hydroxydihydrostrychnine (Wieland and Kaziro, A., 1933, 1175) confirms the conclusions of Leuchs and Beyer (A., 1934, 539). H. W.

[**Strychninolone and its derivatives.**] H. LEUCHS (Ber., 1937, 70, [B], 2031-2033).—In criticism of the publication of Kotake and Mitsuwa (A., 1936, 870) it is suggested that their γ -isomeride is the *c*-form of Leuchs; the ϵ -isomeride is impure δ -form and their β -prep. is a mixture. The δ -substance does not appear to be a strychninolone isomeride. H. W.

Structure of bromomorphine. L. SMALL and S. G. TURNBULL (J. Amer. Chem. Soc., 1937, 59, 1541-1548).—Bromination of morphine, codeine, and various derivatives is shown to occur in position 1 by degradation of bromocodeine (I) to 1-bromodimethylmorphol (1-bromo-3:4-dimethoxyphenanthrene) (II), which, together with its 2-Br-isomeride, is synthesised. The structure of ψ -morphine, however, remains in doubt, as it could not be obtained from bromomorphine. Bromoacetylmethylmorphol [from (I) by Hofmann degradation and acetolysis of the methine] is stable to aq. alkali, but with hot 15% $KOH-MeOH$ gives bromomethylmorphol (1-bromo-4-hydroxy-3-methoxyphenanthrene), m.p. $141.5-142.5^\circ$; this is too sensitive to alkali to be methylated, but the reaction mixture obtained during hydrolysis of its Ac derivative yields (Me_2SO_4) (II), an oil (*picrate*, m.p. $113-115^\circ$; *stypbate*, m.p. $105-108^\circ$). 3:4:6-(OMe) $_2C_6H_2Br \cdot CHO$ and $KOH-MeOH$ give the corresponding acid, m.p. $174-178^\circ$, and alcohol, m.p. $91-94^\circ$; the latter product with HCl in C_6H_6 gives 6-bromoveratryl chloride, m.p. $66.5-68.5^\circ$, and thence the oily *cyanide* and 6-bromohomoveratric acid, m.p. $114-116^\circ$; condensation with *o*-NO $_2 \cdot C_6H_4 \cdot CHO$ and reduction gives 2-amino- α -6'-bromo-3':4'-dimethoxyphenylcinnamic acid; diazotisation and treatment with Naturkupper-C eliminates Br, but Gattermann's Cu paste gives 1-bromo-3:4-dimethoxyphenanthrene-10-carboxylic acid; dry distillation of this acid gives an oily substance, (?) the *Me* ester (*picrate*, m.p. $113-$

115°), not identical with (II), and decarboxylation with Cu eliminates the Br.

3:4:6:2-(OMe) $_2C_6HBr(NO_2) \cdot CHO$ and $CH_2Ph \cdot CO_2Na$ in Ac_2O at 100° give 30% of 6-bromo-2-nitro-3:4-dimethoxy- α -phenyl-, m.p. $206-208^\circ$, and 12% of 6-bromo-2-nitro-3:4-dimethoxy-cinnamic acid, m.p. $200-201^\circ$, and thence $(FeSO_4-NH_3)$ the NH_2 -acids, m.p. $202-203^\circ$ and $150-151^\circ$, respectively, catalytic hydrogenation of which gives Br-free substances, m.p. $169-170^\circ$ and $120-122^\circ$, respectively; the first-mentioned NH_2 -acid, when treated with $BuNO_2$ and $HCl-EtOH$ and then with Cu paste, gives 1-bromo-3:4-dimethoxyphenanthrene-9-carboxylic acid, decomp. $260-270^\circ$, converted by distillation at 75 mm. into the *Me* ester, m.p. $123.5-125^\circ$ (no *picrate*), and by Cu paste in quinoline at 240° into (II). By a similar series of reactions 5-bromo-2-nitroveratraldehyde (prep. from the vanillin derivative), m.p. $70-72.5^\circ$, affords 5-bromo-2-nitro-, m.p. $231-231.5^\circ$, and 2-amino-3:4-dimethoxy- α -phenylcinnamic acid, m.p. $175-176^\circ$ (decomp.), 2-bromo-3:4-dimethoxyphenanthrene-9-carboxylic acid, m.p. $237.5-238.5^\circ$, the *Me* ester, m.p. $114-116^\circ$ (obtained by pyrolysis or CH_2N_2), of which with $H_2-Pd-BaSO_4$ gives *Me* 3:4-dimethoxyphenanthrene-9-carboxylate, m.p. $95-96^\circ$; decarboxylation of the acid gives 2-bromo-3:4-dimethoxyphenanthrene, m.p. $78.5-79.5^\circ$. Bromochlorocodide [from (I) and PCl_5 in $CHCl_3$], m.p. $131-133.5^\circ$, $[\alpha]_D^{25} -288.5^\circ$ in $EtOH$, is reduced by Zn dust- $EtOH-CO_2$ to bromodeoxycodine-C (III), m.p. $210-212.5^\circ$, $[\alpha]_D^{25} +65.9^\circ$ in $EtOH$ (*perchlorate*, m.p. $208-210^\circ$), cryptophenolic, which absorbs $2 H_2$ (Adams) in $EtOH$ to give bromotetrahydrodeoxycodine, form, $+H_2O$, m.p. $119-128^\circ$, $[\alpha]_D^{25} -28.2^\circ$ in $EtOH$; the



methomethylsulphate, m.p. $197-212^\circ$, with $5N-NaOH$ gives, in one step, bromomethylmorphol, m.p. $119-120^\circ$, debrominated by $H_2-Pd-CaCO_3$ to methylmorphol. Deoxycodine-C and Br in aq. $AcOH$ give a *perbromide*, $C_{18}H_{20}O_2NBr_3$, m.p. $184.5-185.5^\circ$, $[\alpha]_D^{25} -156.7^\circ$ in C_6H_6 , hydrogenated (Adams) in $EtOH$ to a new phenolic bromotetrahydrodeoxycodine (*hydrobromide*, m.p. $116-117.5^\circ$, $[\alpha]_D^{25} -3.3^\circ$ in $EtOH$), which with $Na-EtOH$ gives a Br-free phenolic substance (C 72.5, H 7.9%), m.p. $88-89^\circ$. Deoxycodine-A or its hydrobromide with Br in $AcOH$ gives a substance, m.p. $189-189.5^\circ$, $[\alpha]_D^{25} +10.2^\circ$ in C_6H_6 (contains 2 Br; *hydrobromide*, m.p. $149-151^\circ$, $[\alpha]_D^{25} -3.8^\circ$ in $EtOH$), which with hot $NaOAc-Ac_2O$ gives 1-bromoacetylmethylmorphol. Dihydrodeoxycodine-D with Br- $AcOH$ or aq. Br- $AcOH$ gives a Br-derivative, m.p. $156-157^\circ$, $[\alpha]_D^{25} -37.6^\circ$ in $EtOH$.

R. S. C.

Curare alkaloids. III. Pot-curare. H. KING (J.C.S., 1937, 1472-1482).—By extraction with 1% tartaric acid, the alkaloids of a specimen of pot-curare have been separated into "non-quaternary" bases (38%) and "quaternary" bases (12%). The paralyzing dose on frogs under standard conditions has been determined, and, although the former frac-

tion shows weak curare action, most of the activity lies in the "quaternary" fraction. The "non-quaternary" bases may be separated into *protocuridine* (I), $C_{36}H_{38}O_6N_2$ (+0.5C₅H₅N), m.p. 295° [dihydrochloride (+6H₂O), m.p. 295° (efferv.), $[\alpha]_{D}^{20} +7.6^\circ$ in H₂O; *O*-methylprotocuridine methiodide, m.p. 318° (decomp.)] (cf. Boehm, A., 1898, i, 283), and *neoprotocuridine* (II), $C_{36}H_{38}O_6N_2$ (+8H₂O), m.p. 232° (efferv.) [dihydrochloride (+6 or 7 H₂O), m.p. >310°; *O*-methylneoprotocuridine methiodide, m.p. >300°]. The Millon reaction is shown by (I) but not by (II). From the "quaternary" fraction, (II) has been isolated as hydrochloride and also a mixture of alkaloids from which an amorphous iodide of high paralyzing activity and showing a Millon reaction has been separated. By methylation of fractions of the alkaloids, *iodide A*, $C_{20}H_{25}O_8NI_2$, m.p. 260° (decomp.), and *iodide B*, $C_{17 \text{ or } 18}H_{22}O_2NI$, m.p. 318°, have been obtained. (II) has been identified as an internally compensated form of *isochondrodendrine*; this establishes a close relationship between the alkaloids of *pot-curare* and those of *tubecurare*, as both are based on the fusion of two polyphenolic benzylisoquinoline nuclei by ether linkages. The botanical origin is discussed. F. R. S.

Sinomenium and Cocculus alkaloids. XLVI. **Methylisochondrodendrine.** H. KONDO, M. TOMITA, and S. UYEO (Ber., 1937, 70, [B], 1890—1893).—Chromatographic analysis (Al₂O₃, Brockmann) of the crude bases from *Cissampelos insularis*, Makino, does not lead to the isolation of insularine but yields methylisochondrodendrine, also obtained from *Stephania cepharantha*, Hayata. Its identity with the product of Faltis (A., 1934, 423) is established by direct comparison of the alkaloids, their methine and hydromethine bases. H. W.

***m*-Arsenated phenoxyethanols.** S. B. BINKLEY and C. S. HAMILTON (J. Amer. Chem. Soc., 1937, 59, 1716—1719).—*m*-OH·C₆H₄·AsO₃H₂ does not condense with CH₂Cl·CH₂·OH, but *m*-NO₂·C₆H₄·OH in 2N-NaOH gives β -*m*-nitrophenoxyethyl alcohol, m.p. 88°, reduced (H₂-Raney Ni) to *m*- β -hydroxyethyl-aniline, m.p. 52°, which affords (Bart) *m*- β -hydroxyethylphenylarsinic acid, m.p. 110° (Na salt). With HNO₃ (d 1.5) this gives a mixture of nitrates, hydrolysed by hot 3N-HCl to 2-, m.p. 270° (I), and 4-nitro- β -hydroxyethylphenylarsinic acid (II), m.p. 164°, which afford (SO₂-HI) the corresponding *arsinoxides*, m.p. >270°, and thence by Hg(OAc)₂ β -2-nitro-3-, m.p. 150—152°, and β -2-nitro-5-chloromercuriphenoxyethyl alcohol, m.p. 147—149°, both of which with 3N-HCl give *o*-NO₂·C₆H₄·O·CH₂·CH₂·OH, hydrolysed by 6N-NaOH to *o*-NO₂·C₆H₄·OH. With 6N-NaOH (I) and (II) give 2-, m.p. 208° (decomp.), and 4-nitro-3-hydroxyphenylarsinic acid, m.p. >270°; the 2-NO₂-acid affords successively 2-nitro-3-hydroxyphenylarsinoxide, m.p. 220—223° (decomp.), 2-nitro-3-chloromercuriphenol, m.p. 212—214°, and 2:3-NO₂·C₆H₃I·OH. R. S. C.

Arsenic derivatives of 1:4-benzisoxazine.—See B., 1937, 1136.

Organo-arsenic compounds. V. Synthesis of arsindole derivatives. H. N. DAS-GUPTA (J.

Indian Chem. Soc., 1937, 14, 349—353).—C₂H₂ and AlCl₃ convert AsPhCl₂ into a mixture of diphenyl- β -chlorovinyl-, phenyl- β '-dichlorodivinyl- (also synthesised from the chloroarsine and MgPhBr) (*double salts* with HgCl₂, m.p. 157—158°, and AgNO₃, m.p. 170°; *methiodide*, m.p. 232°), and phenyl- β -chlorovinylchloroarsine (cf. J.C.S., 1925, 127, 996). The last has been converted into the corresponding *arsinic acid*, m.p. 135°, *Et ether*, b.p. 165—170°/3 mm., *arsenious cyanide*, and *sulphide*, m.p. 141°, and by Grignard reagents into the phenyl- and methylarsines. When treated with AlCl₃ in CS₂ or heated to 230°, it affords 1-chloroarsindole. A. L.

Mercury compounds of benzotrifluoride.—See B., 1937, 1136.

Mercuriation of benzanthrone(-7). A. BERNARDI (Gazzetta, 1937, 67, 380—384).—Benzanthrone(-7) with Hg(OAc)₂ at 171° yields its 3-*mercuriacetate* (I), which at its m.p., 141—142°, gives *Hg bisbenzanthranyl*, m.p. 70—75°. 0.1N-KOH-EtOH converts (I) into the 3-*mercurihydroxide*, decomp. 260° (*chloride* prepared). With Br-KBr in AcOH, (I) forms 3-bromobenzanthrone(-7). E. W. W.

The cyclol hypothesis and the "globular" proteins. D. M. WRINCH (Proc. Roy. Soc., 1937, A, 161, 505—524).—A further development of the "cyclol" hypothesis (cf. this vol., 394). The general "cyclol" fabric, consisting of hexagonal rings, is folded according to geometrical rules to produce closed "globular" mols. It is shown that several systems can exist, the series formed by folding the cyclol network on to the faces of a truncated tetrahedron being here described. This series consists of a no. of mols. C₁, C₂ . . . C_n in which the no. of NH₂-acid radicals is 72, 288 . . . 72n². It is suggested that the group of proteins with mol. wts. 33,600—40,500 are represented by closed "cyclols" of the type C₂ containing 288 residues. The ionic behaviour of such mols. in solution is discussed with particular reference to reversible association and the hydration of the mol. G. D. P.

Ultracentrifugal purification and study of macromolecular proteins. R. W. G. WYCKOFF (Science, 1937, 86, 92—95).—A review. L. S. T.

Clupein. VIII. K. FELIX and A. MAGER (Z. physiol. Chem., 1937, 249, 111—123; cf. A., 1933, 963; Waldschmidt-Leitz and Kofrany, A., 1936, 110).—The hydrochloride (I) of the Me ester of clupein (II) contains total N 24.99, Cl 16.08, and OMe 0.65%. The N is distributed as follows: as arginine (III) 89.39, (NH₂)-acid 11.4, alanine (IV) 1.84, serine (V) 1.73, NH 3.76, and valine (VI) 3.67. Arginylarginine and oxyproline (VII) are obtained as picrates from (I). The nos. of residues of (III), (IV), (V), (VII), and (VI) + others in (II) are 22, 2, 2, 1, and 3, respectively, and the no. of proline residues is 3. The mol. wts. of (II) and its Me ester are 4470 and 5340, respectively. The (II) formula previously suggested is modified in the light of these results. W. McC.

Rapid method for protein dialysis.—See A., III, 447.

Green derivative of hæmoglobin.—See A., III, 370.

Semi-micro methods for determining the elements in organic analysis. H. BERGER (Chem. Fabr., 1937, 10, 396—398).—A thermostatically controlled electric furnace is preferred for heating the tubes, and in the determination of halogens and S, as well as C, H, and N, the temp. is maintained at 700°. PbO_2 is superior to Cu for removing N oxides. A special Kipp apparatus for preparing air-free CO_2 is described. A bead tube is used for the determination of halogens and S.

I. C. R.

Determination of nitrogen and carbon in the same sample. C. T. GAYLEY (Ind. Eng. Chem. [Anal.], 1937, 9, 422—423).—The gases formed during a Kjeldahl N determination are passed in a stream of O_2 over Pt gauze in an electric furnace, cooled, and passed successively through $\text{K}_2\text{Cr}_2\text{O}_7$, 10% H_2SO_4 , Zn, conc. H_2SO_4 , and Dehydrite; finally the CO_2 is absorbed and weighed.

R. S. C.

Determination of iodine in organic substances. H. DOERING (Ber., 1937, 70, [B], 1887—1889).—In the customary Carius procedure AgNO_3 is replaced by $\text{Hg}(\text{NO}_3)_2$ and the vol. of HNO_3 is increased to 5 c.c. The contents of the bomb tube are treated with aq. CaOCl_2 , whereby I is converted into HIO_3 . Excess of Cl is removed by cautious addition of HCO_2Na , the mixture is cooled, and solid KI is added. The liberated I is titrated with $\text{Na}_2\text{S}_2\text{O}_3$ in presence of starch.

H. W.

Simultaneous determination of chlorine, nitrogen, and arsenic in organo-arsenic compounds. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1937, 14, 358—361).—The compound is slowly heated with a mixture of K_2SO_4 , conc. H_2SO_4 , and a little Se. The gaseous chlorides are absorbed in alkaline H_2O_2 , and the Cl is determined volumetrically, or gravimetrically after boiling, treating with NaHSO_3 , and acidifying. The NH_3 in the residue is expelled by NaOH and the remaining solution treated with NaHSO_3 , acidified, boiled, and the As determined with I.

A. Li.

Semi-micro-determination of arsenic in organic compounds. E. I. AIZENSCHTADT (Zavod. Lab., 1937, 6, 503—504).—10 mg. of substance are heated with 0.5 ml. of H_2O and 1 ml. of H_2SO_4 (4 min. at the b.p.), 1 ml. of H_2O is added, and boiling is continued until SO_3 fumes appear. This operation is repeated, the solution is washed into a flask by means of 5 ml. of 20% H_2SO_4 , 5 ml. of 10% KI and 30 ml. of H_2O are added, and the solution is titrated with 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$ after 15 min. The vol. of $\text{Na}_2\text{S}_2\text{O}_3$ required in a blank test is subtracted, and the As content is hence calc.

R. T.

Determination of arsenic in mineral oil solutions.—See A., I, 579.

Volumetric determination of mercury [in organic compounds]. M. FITZGIBBON (Analyst, 1937, 62, 654—656).—Org. Hg compounds are destroyed by heating with H_2SO_4 . An excess of KI is added, and the solution is made alkaline with NaOH. 40% aq. CH_2O is added at 60°, together with 2.5% aq. gelatin to stabilise the reduced Hg in colloidal suspension. The solution is cooled to 20°, acidified with

AcOH, and treated with 0.1N-I, the excess of I being finally titrated back.

J. S. A.

Determination of tellurium in organic compounds. E. T. TSAO (Chem. Ind. [China], 1935, 10, No. 2, 15—21).—0.2—0.3 g. of the Te compound is fused with 14 g. of Na_2O_2 , 0.1 g. of KClO_3 , and 0.2—0.3 g. of sucrose in a Parr bomb. The product is dissolved in H_2O , boiled to remove peroxide, acidified with HCl, and conc. to 100 c.c., 30 c.c. of 12N-HCl are added, and the solution is heated to boiling. 15 c.c. of saturated aq. SO_2 , 10 c.c. of 15% $\text{N}_2\text{H}_4\cdot\text{HCl}$, and a further 15 c.c. of saturated aq. SO_2 are added and the solution is boiled and filtered on a Gooch crucible. The ppt. of Te is washed with H_2O and EtOH and dried at 105°.

CH. ABS. (e)

Physical method of drying liquefied hydrocarbons. E. E. ROPER (Ind. Eng. Chem. [Anal.], 1937, 9, 414—415).—0.7 mg. of H_2O in 100 g. of $\text{CH}_2\text{Cl}_2\text{CMe}_2$ is detectable as a turbidity when the liquid is cooled to -80° . An apparatus for drying hydrocarbons is described. The liquid is placed over glass wool in a closed system at -80° ; the wool rests over a capillary tube passing into a vessel containing the hydrocarbon at -135° . Passage of liquid through the wool filter is caused by the difference in v.p. of the liquid at the two temp.

R. S. C.

Determination of methoxyl. F. ARNDT and F. NEUMANN (Ber., 1937, 70 [B], 1835).—The method of gradual heating advised for highly methylated carbohydrates by Neumann (this vol., 229) has been applied in other circumstances by Arndt (*ibid.*, 283) and thus appears generally useful.

H. W.

Microchemical detection of organic compounds by means of drop reactions. F. FEIGL [with A. LENZER, V. DEMANT, O. FREHDEN, and V. ANGER] (Mikrochim. Acta, 1937, 1, 127—141).—(a) Sulphinic acids, sulphonic acids, or sulphones are detected by fusion with NaOH, forming Na_2SO_3 . On acidification, the SO_2 liberated induces the oxidation of $\text{Ni}(\text{OH})_2$ spread on a slip of filter-paper, which may be impregnated with benzidine (purple colour produced) to increase the sensitivity. (b) NH_2OH and oximes in 1 drop of solution are treated successively with NaOAc, 1% sulphanilic acid (I) in dil. AcOH, and 0.1N-I in glacial AcOH. NH_2OH is oxidised to HNO_2 , which diazotises (I). On addition of $\text{Na}_2\text{S}_2\text{O}_3$ and then 0.3% $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ (II) in dil. AcOH, a red coloration is produced with 10^{-8} g. of NH_2OH . Oximes are first hydrolysed by warming with HCl before treatment as above. (c) Arylhydrazines, -hydrazones, and -osazones are oxidised to diazo-salts by treatment with a drop of HCl + solid SeO_2 . On addition of (II), red to violet colorations are produced. (d) Glycerol and glycerides are heated with KHSO_4 , forming acraldehyde, which gives a blue coloration on paper impregnated with *o*-dianisidine or, better, with $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] + \text{piperidine}$. Limit, 0.005 mg. (e) *sec.* Aliphatic amines in neutral aq. solution are treated with a drop of aq. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ containing 10% of MeCHO. Addition of Na_2CO_3 gives a blue to violet colour.

J. S. A.

Determination of acetone, *n*-butyl and ethyl alcohol, present together. I. **Oxidation method.** M. N. BECHTEREVA and N. D. JERUSALIMSKI (J. Appl. Chem. Russ., 1937, 10, 1314—1320).— COMe_2 is determined in a COMe_2 -BuOH-EtOH- H_2O mixture by the CHI_3 method; a second portion of the mixture is oxidised by Osburn and Werkman's method (B., 1931, 1117), and the acids produced are determined by the method of Virtanen and Pulkki (B., 1928, 688), applying a correction for AcOH produced by oxidation of COMe_2 (8% of the no. of ml. of 0.1N- COMe_2 present). R. T.

Microchemical determination of butyric acid. L. KLING (Mikrochem., 1937, 23, 60—61; cf. A., 1936, 1397).—In the method previously described distillation is preferably carried out in apparatus with ground joints. The H_2O_2 should be prepared from Na_2O_2 and 2N- H_2SO_4 . The flame must be low during distillation to prevent H_2O_2 passing into the distillate. Preferably the test sample should contain 0.05—2.0 mg. of PrCO_2H . J. W. S.

Quantitative micro-analysis of mixtures of fumaric and maleic acid. G. SEMERANO and I. S. RAO (Mikrochem., 1937, 23, 9—16).—The determination of maleic (I) and fumaric (II) acid in presence of one another through the difference in their reduction potentials (A., 1932, 1234) has been adapted to the microchemical scale. For determination of (I), the K salts are dissolved in aq. NH_4Cl , and for determination of (II) the Li salts are dissolved in LiCl . The reduction potentials under these conditions are, according to concn., between -1.90 and -1.26 v. for (I) and between -1.90 and -1.84 v. for (II). The heights of the waves in the polarographic diagrams \propto the concns. With quantities $>10^{-6}$ g. the accuracy is $\pm 1\%$. J. W. S.

Volumetric analytical notes. [Determination of chloral hydrate, hypophosphite, phosphite, halogen oxyacids, and phenol.] A. SCHWICKER (Z. anal. Chem., 1937, 110, 161—184).—(i) Chloral hydrate may be determined (a) iodometrically, in the presence of NH_4 borate. (b) Bromometrically, by adding an excess of 0.1N- $\text{KBrO}_3 + \text{KBr} + \text{conc. HCl}$, and then borax. The excess of free Br is finally titrated back with AsO_3''' . (c) By oxidation with an excess of 0.1N- KMnO_4 in Na_2CO_3 -alkaline solution; excess of KMnO_4 is determined iodometrically. (d) By hydrolysis to $\text{CHCl}_3 + \text{HCO}_2\text{Na}$ by means of NaOH at 100° . An equal vol. of saturated aq. NaOAc is added, and the HCO_2Na is titrated at 80° with KMnO_4 . (e) By reduction to Cl' with Zn dust + 10% $(\text{NH}_4)_2\text{SO}_4$. The Cl' is then titrated with AgNO_3 .

(ii) (a) $\text{H}_2\text{PO}_2'$ reduces HgCl_2 to Hg_2Cl_2 ; the first stage proceeds in HCl solution, but is completed rapidly only in neutral solution. The final solution is acidified with HCl, and Hg_2Cl_2 is dissolved in an excess of 0.1N- KBrO_3 , which is finally titrated back with AsO_3''' . $\text{H}_2\text{PO}_3'$ reduces HgCl_2 in neutral solution and may be determined similarly. (b) $\text{H}_2\text{PO}_2'$ may be determined also with KMnO_4 , the excess of which is titrated back iodometrically, or with $\text{H}_2\text{C}_2\text{O}_4$; (c) by oxidation with KBrO_3 in H_2SO_4 solution at 100° ; or (d) with $\text{KBrO}_3 + \text{KBr}$ or

$\text{KBrO}_3 + \text{HCl}$. $\text{H}_2\text{PO}_3'$ is oxidised with $\text{KBrO}_3 + \text{KBr}$ in hot solution, or with NaOCl in a solution neutralised with NaHCO_3 .

(iii) BrO_3' and IO_3' together are determined (a) by iodometric titration of total $\text{BrO}_3' + \text{IO}_3'$; (b) BrO_3' in a separate sample is destroyed by means of HCl, the Br and Cl liberated being bound by addition of PhOH; IO_3' is then determined independently. I' can be selectively oxidised to IO_3' in the presence of Br' by means of OCl' in Na_2CO_3 solution, the IO_3' being finally determined iodometrically. IO_3' in presence of BrO_3' is determined by complete reduction to I' and Br' by means of KHSO_5 . I' is then oxidised to IO_3' with OCl' and determined as above. For the determination of I' , IO_3' , and BrO_3' together, I' is determined with standard NaOCl . $\text{IO}_3' + \text{BrO}_3'$ in a separate sample are determined iodometrically, and $\text{I}' + \text{IO}_3'$ are finally determined with OCl' after reduction with KHSO_5 . Alternatively, I' is oxidised to IO_3' , and total IO_3' is determined after destruction of BrO_3' with HCl. I' in presence of Br' is oxidised to IO_3' by a slight excess of 0.1N- KMnO_4 at 80° . The excess of KMnO_4 is destroyed with EtOH, the solution filtered from MnO_2 , and the IO_3' in an aliquot part is determined iodometrically. IO_4' in the presence of IO_3' is determined by reducing IO_4' to IO_3' by means of H_2O_2 in alkaline solution. The excess of H_2O_2 is destroyed by boiling, and the total IO_3' is determined iodometrically. $\text{IO}_4' + \text{IO}_3'$ in a separate portion is determined by titration of the total I liberated with $\text{KI} + \text{HCl}$.

(iv) PhOH is determined by the direct titration of an HCl solution, containing KBr, with 0.1N- KBrO_3 . The excess of KBrO_3 is titrated back with AsO_3''' .

J. S. A.

Volumetric determination of semicarbazide and aminoguanidine. G. S. SMITH (J.C.S., 1937, 1325).— N_2H_4 derivatives are determined by treatment of the hydrochloride or sulphate with KIO_3 , KI, and H_2SO_4 , followed by determination of the residual I. The guanidine or semicarbazide content is calc. from the reactions $5\text{NHR}\cdot\text{NH}_2 + 4\text{KIO}_3 \rightarrow 2\text{I}_2$ and $\text{KIO}_3 + 5\text{KI} \rightarrow 3\text{I}_2$. J. D. R.

Extractor for monoamino-acids. D. W. WOOLLEY (Ind. Eng. Chem. [Anal.], 1937, 9, 433).—An apparatus is described for extraction of NH_2 -acids (or other heat-labile substances) without their anhydrides from neutral aq. solution by boiling BuOH ($50^\circ/\text{vac.}$). Only the upper part of the BuOH is heated; the acids crystallise from the cold part and are not subjected to heat. R. S. C.

Effect of aldehydes on the determination of cysteine and cystine. M. X. SULLIVAN and W. C. HESS (J. Biol. Chem., 1937, 120, 537—542).—The effect of adding varying amounts of CH_2O (I), MeCHO (II), $(\text{CHO})_2$, AcCHO , and $\text{C}_6\text{H}_{13}\text{CHO}$ (III) on the accuracy of various methods of determining cysteine (IV) and cystine (V) is examined. Freshly added aldehydes have little effect in the Sullivan (A., 1930, 199) and Okuda (A., 1926, 190) methods for (V). The Folin-Marenzi method (A., 1929, 1093) for (V) is inhibited markedly by (I), somewhat by (III), but only slightly by (II). For (IV), aldehydes

have little effect on the Okuda method, some effect in the Sullivan and Folin-Marenzi methods, and marked inhibiting effect in the Mason method (cf. A., 1930, 803).
E. W. W.

Determination of thiol and disulphide compounds, with special reference to cysteine and cystine. VIII. Molecular ratio between *A*-phospho-18-tungstic acid and cysteine in their colour reaction. K. SHINOHARA (J. Biol. Chem., 1937, 120, 743—749).—*A*-Phospho-18-tungstic acid, new formula for crystals $P_2O_5(WO_3)_{18} \cdot 26H_2O$ (I) (cf. A., 1920, ii, 625), does not react regularly with 2RSH (cf. A., 1935, 877, 1111; 1936, 60, 353). With cysteine (II) and (I) or its $(NH_4)_6$ salt, at pH 5, in a first reaction (I) loses 1 equiv. of O per mol. of (II), but with excess of (II), (I) slowly loses a second equiv. of O. Colour intensity is plotted against time under varying conditions; it is const. only at pH 4.7—7.5, and in presence of excess of (I).
E. W. W.

Applicability of Benedict-Denis procedure to determination of methionine-sulphur. C. B. RUTENBER and J. C. ANDREWS (J. Biol. Chem., 1937, 120, 203—207).—Addition of 10 m.-equiv. of Na_2CO_3 to 10 ml. of Benedict-Denis reagent gave maximal (95.6%) recovery of S in determination of methionine. Larger or smaller amounts of Na_2CO_3 lower the S recovery. Prolonged ignition after evaporation is without advantage.
J. L. C.

Determination of nitrogen by hydrogenation in betaine, pyramidone, and sulphanilic acid. H. TER MEULEN and H. J. RAVENSWAAY (Rec. trav. chim., 1937, 56, 1022—1023).—N can be determined accurately in these compounds by hydrogenation.
H. W.

Titration of aromatic amines with nitrous acid. J. PHILLIPS and A. LOWY (Ind. Eng. Chem. [Anal.], 1937, 9, 381—382).—2:4:6- $(NH_2)_3C_6H_2 \cdot CO_2H$, 1:2:4:6- $C_6H_2Me(NH_2)_3$, 1:3:5- $C_6H_3(NH_2)_3$, 1:2:4:6- $C_6H_2Cl(NH_2)_3$, metanilic acid, *m*- $C_6H_4(NH_2)_2$, and 1:2:4- $C_6H_3Me(NH_2)_2$ can be determined by addition of excess of $NaNO_2$ to the HCl solution followed by back-titration with either $NH_2Ph \cdot HCl$ or sulphanilic acid. Titration of 2:4:6- $(NH_2)_3C_6H_2 \cdot OH$, 1:2:4- $C_6H_3(NH_2)_3$, and *o*- and *p*- $C_6H_4(NH_2)_2$ does not give quant. results.
E. H. S.

New photo-reaction of pyridine. A. CASTIGLIONI (Annali Chim. Appl., 1937, 27, 256—257).—Filter-paper soaked in a 1% EtOH solution of quinoline (I), treated with a 0.05% aq. solution of C_5H_5N , and exposed to ultraviolet light, slowly develops a yellow coloration. Using lepidine instead of (I), a similar colour results, and a less intense colour using quinaldine, hydroxyquinoline, isquinoline, or acridine. The reaction can be used to detect C_5H_5N in presence of nicotine, since with (I) the latter slowly gives only a greyish coloration.
E. W. W.

Determination of pyridine in presence of pyridine homologues. L. BARTA and Z. MARSCHEK (Biochem. Z., 1937, 293, 118—120).— C_5H_5N homo-

logues (α - and β -picoline, α' -lutidine, *s*-collidine) and piperidine give with BrCN and β - $C_{10}H_7 \cdot NH_2$ a red colour similar to that given by C_5H_5N but the colour is usually 50—90 times weaker and the error in the colorimetric determination of C_5H_5N in presence of five times the amount of homologue is 8—10%. Distillation with citrate buffer enables C_5H_5N and its homologues to be separated from NH_3 and nicotine.
P. W. C.

Highly sensitive and specific microchemical reactions of sparteine with cobalt and iron salts. A. MARTINI (Mikrochim. Acta, 1937, 1, 164—167).—Cryst. ppts. of characteristic habit are formed with $NH_4CNS + Co$ or Fe^{+++} salts.
J. S. A.

Identification and differentiation of ephedrine and ψ -ephedrine. P. FOURMENT and H. ROQUES (Bull. Sci. Pharmacol., 1937, 44, 372—375).—Ephedrine can be accurately determined by the formation of CHI_3 on adding hypoiodite. It immediately gives with alkaline OsO_4 an orange ppt. which gives a violet coloration with boiling HCl, whereas ψ -ephedrine gives slowly a yellowish ppt. followed by a yellow coloration with HCl.
E. M. W.

Reaction of morphine with vanillin and hydrochloric acid. Different action of some aromatic aldehydes on morphine and ψ -morphine. B. DREVON (J. Pharm. Chim., 1937, [viii], 26, 292—299).— ψ -Morphine (I) with vanillin-HCl at 100° gives a green coloration (cf. this vol., 268). The reaction is given by many aromatic aldehydes in the nucleus of which OH, Me, NO_2 , and CH_2O_2 are substituents. Morphine and (I) give different colours. Furfuraldehyde and glucose do not serve as aldehydes.
J. L. D.

The biuret reaction. IV. Combination of copper, nickel, and cobalt with proteins. H. JESSERER and F. LIEBEN. V. Biuret reaction of organic substances of low mol. wt. R. KRETSCHMAYER and H. JESSERER (Biochem. Z., 1937, 292, 403—418, 419—423; cf. A., 1936, 1398).—Alkaline aq. caseinogen (I) combines stoichiometrically with Cu, Ni, and Co (as hydroxides) to give violet, golden-yellow, and red-brown coloured derivatives, respectively, dialysis of which yields a blue neutral Cu derivative of equal Cu content and a neutral Co derivative of the same colour and Co content, the Ni compound being decomposed to $Ni(OH)_2$. Compounds of Cu, Ni, and Co with zein, edestin, fibrin, gelatin, and Witte's, silk-, and (I)-peptone were investigated. The compounds with peptones are less defined than those with proteins; Ni in the latter is bi- and Co ter-valent. The presence of the metal prevents *N*-methylation, whilst the methylated proteins behave abnormally only with Ni. The metals probably combine at the peptide linking. No reaction occurs between Fe and proteins.

V. The "biuret reaction" is given by arginamide and arginine anhydride but not by histidine, succinimide, serine, colamine, arginine, and α -benzoyl-arginine. At least two adjacent $CO \cdot NH_2$, $CS \cdot NH_2$ or $C(NH) \cdot NH_2$ groups are essential for the reaction.
F. O. H.

BRITISH CHEMICAL ABSTRACTS

A., II.—Organic Chemistry

DECEMBER, 1937.



Chain vibrations of isomeric paraffins and their identification in the Raman spectrum.—See A., I, 549.

Oxidation of propane.—See A., I, 621.

Paraffin hydrocarbons from crude synthetic isooctane [$\beta\beta\delta$ -trimethylpentane]. D. B. BROOKS, R. B. CLEATON, and F. R. CARTER (J. Res. Nat. Bur. Stand., 1937, 19, 319—337).—The following hydrocarbons have been isolated from crude isooctane, partly by distillation and partly by crystallisation from CH_4 : $\beta\beta$ - and $\beta\gamma$ -dimethylbutane; β -methyl-, $\beta\beta$ -, $\beta\gamma$ -, $\beta\delta$ -dimethyl-, $\beta\gamma\gamma$ - and $\beta\gamma\delta$ -trimethylpentane; β -methyl-, $\beta\delta$ -, $\beta\epsilon$ -, $\delta\epsilon$ -dimethyl-, $\beta\beta\delta$ -, $\beta\beta\epsilon$ -trimethyl-, $\gamma\gamma\delta\delta$ -tetramethyl-, and $\beta\beta\gamma\gamma\delta$ -penta-methyl-hexane; $\beta\delta$ -, $\gamma\gamma$ -dimethyl-, δ -ethyl-, $\beta\beta\zeta$ -, $\beta\beta\delta$ -(or $\beta\beta\epsilon$)-trimethyl-heptane; $\beta\zeta$ -dimethyloctane. The majority of these are present to the extent of <0.05%. F. L. U.

Reaction for unsaturated hydrocarbons or their peroxides. E. LEDERER (Petroleum, 1937, 33, No. 38, 9—13).—When treated with the heavy-metal salts of certain aliphatic, hydroaromatic, or aromatic carboxylic and sulphonic acids, e.g., Mn or Co octoate or stearate, unsaturated hydrocarbons give a characteristic colour change, e.g., from colourless to deep brown in the case of the Mn salts. Development of the colour forms a delicate test for the presence of unsaturated compounds, the test being carried out by treating 0.5—1 c.c. of the oil with 10 mg. of the Mn salt and heating the mixture for 10 min. on the steam bath. The reaction is dependent on the presence of a peroxide of the unsaturated compound. The reaction may be used to free the oil from peroxides. Colour changes occurring when certain (particularly polynuclear) hydrocarbons are treated with Ag salts are due to another type of reaction, viz., a reduction with separation of colloidal Ag.

A. B. M.

Photochemical chlorination of ethylene compounds.—See A., I, 627.

Polymerisation of isoprene. W. H. CARMODY and M. O. CARMODY (J. Amer. Chem. Soc., 1937, 59, 2073—2074).—Vapour-phase polymerisation of isoprene over AlCl_3 gives exclusively a sol. polymeride, the mol. wt. (1300 in C_6H_6) of which is approx. twice that of the product formed during liquid-phase polymerisation (A., 1932, 830). H. B.

Pyrolysis of isobutene at very low conversions. C. D. HURD and F. H. BLUNCK (J. Amer. Chem. Soc., 1937, 59, 1869—1871).—Decomp. of isobutene at 650° to the extent of 0.1—1% gives CH_4 (50—59),

C_2H_4 (11—13.6), and C_3H_6 (29—36%) as the only gaseous products. The persistence of C_2H_4 emphasises the need for caution in interpreting the method of extrapolating products formed during such decomp. to their vals. at zero conversion. H. B.

$\beta\epsilon\epsilon$ -Trimethyl- $\Delta^{\alpha\gamma}$ -hexadiene and its hydrogen bromide additive product. K. N. CAMPBELL (J. Amer. Chem. Soc., 1937, 59, 1980—1983).—The ketol from $\text{Bu}^\gamma\text{CHO}$ (prep. from $\text{MgBu}^\gamma\text{Cl}$ and HCO_2Me) and COMe_2 in EtOH - NaOEt is dehydrated (distillation with I) to β -keto- $\epsilon\epsilon$ -dimethyl- Δ^γ -hexene (I), b.p. 78 — $80^\circ/40$ mm. (2:4-dinitrophenylhydrazine, m.p. 159 — 161° ; semicarbazone, m.p. 178°), which gives an unstable compound with dry HCl . The carbinol from (I) and MgMeCl is similarly dehydrated to $\beta\epsilon\epsilon$ -trimethyl- $\Delta^{\alpha\gamma}$ -hexadiene (II), b.p. $128^\circ/732$ mm., which is reduced catalytically to $\beta\epsilon\epsilon$ -trimethylhexane and by Al-Hg in moist Et_2O to $\beta\epsilon\epsilon$ -trimethyl- Δ^β -hexene (?), b.p. $72^\circ/735$ mm. (ozonolysis products, COMe_2 and $\text{CH}_2\text{Bu}^\gamma\text{CHO}$). (II) and HBr (1 mol.) in cold CHCl_3 give the not very stable β -bromo- $\beta\epsilon\epsilon$ -trimethyl- Δ^γ -hexene (?), b.p. 75 — $77^\circ/50$ mm., oxidised by KMnO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7$ (method: Farmer and Marshall, A., 1931, 460) to $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ and by O_3 (followed by Zn dust and H_2O) to $\text{Bu}^\gamma\text{CHO}$ and (polymeric) $\text{OH}\cdot\text{CMe}_2\cdot\text{CHO}$. $\alpha\beta$ -Addition of HBr , with no rearrangement, thus occurs. H. B.

Peroxide effect in the addition of hydrogen bromide to ethylene compounds. XIV. Addition of hydrogen bromide to the higher alkenes. M. S. KHARASCH and W. M. POTTS (J. Org. Chem., 1937, 2, 195—197).—Addition of HBr to Δ^{α} -nonene, -undecene, -tridecene, and -pentadecene, and to allylbenzene etc., gives primary bromides whenever peroxides are present, and *sec.* bromides in the presence of antioxidants. E. W. W.

Oxidation of unsaturated hydrocarbons by atmospheric oxygen. I. E. AFFERNI (Annali Chim. Appl., 1937, 27, 366—372).—Oxidation of $\text{Me}\cdot[\text{CH}_2]_{13}\cdot\text{CH}\cdot\text{CH}_2$ by air at 125 — 145° , for 40 days, produces a wt. increase of 16.5%, and yields CO and CO_2 , the evolution of which increases to a max. and eventually ceases, a polymerised acid (30%), mol. wt. 730—800, forming an *Et* ester $\text{C}_{17}\text{H}_{34}\text{O}_2$, b.p. $117.5^\circ/15$ mm., and a highly polymerised unsaponifiable residue. No peroxides were detected. L. A. O'N.

Action of elementary fluorine on organic compounds. IV. Vapour-phase fluorination of ethane. J. D. CALFEE and L. A. BIGELOW (J. Amer. Chem. Soc., 1937, 59, 2072—2073; cf. A., 1937, II, 81).— C_2H_6 and F_2 react in the vapour phase

over Cu gauze to give C_2F_6 and smaller amounts of CF_4 , CHF_3 , and $CMeF_3$ (?). H. B.

Kinetics of the pyrolysis of *n*-propyl iodide and *n*-butyl iodide.—See A., I, 621.

Allylic rearrangements. IV. Composition of butenyl bromides prepared from crotyl alcohol and methylvinylcarbinol. W. G. YOUNG and J. F. LANE (J. Amer. Chem. Soc., 1937, 59, 2051—2056).—Mixtures of $CHMe:CH:CH_2Br$ (I) and $CH_2:CH:CHMeBr$ (II) are obtained from either crotyl alcohol or methylvinylcarbinol by treatment with (i) 48% HBr at -15° , (ii) 48% HBr + conc. H_2SO_4 at -15° , (iii) saturated aq. HBr at 0° , (iv) dry HBr at -20° , (v) $PBr_3 + C_6H_5N$ at -15° or -75° . The composition (determined refractometrically and corr. for small amounts of inert impurities) of the mixtures varies with each reagent and with the alcohol used. Since known mixtures of (I) and (II) do not alter appreciably under the experimental conditions used, rearrangements must occur during the formation of the bromides from the alcohols. Considerable rearrangement of (II) into (I) occurs with 48% HBr at 20° . H. B.

Bouveault reaction for the preparation of unsaturated alcohols. G. GOETHALS (Natuurwetensch. Tijds., 1937, 19, 184—188).—Reduction of Me Δ^2 -pentenoate with Na in dry MeOH or EtOH gave a mixture of 25% of amyl alcohol and 75% of Δ^2 -pentenol together with smaller quantities of β - or γ -methoxyvaleric acid, and a very small quantity of β - or γ -methoxy-*n*-amyl alcohol. S. C.

Derivatives of $\beta\beta\beta$ -trialkylethanol. R. V. RICE, G. L. JENKINS, and W. C. HARDEN (J. Amer. Chem. Soc., 1937, 59, 2000).—The *H* phthalates, m.p. $70-71^\circ$, $68-69^\circ$, $44.5-45.5^\circ$, and $84-85^\circ$, *H* tetrachlorophthalates, m.p. $140-141^\circ$, $149.5-150.5^\circ$, $144-145^\circ$, and $138-139^\circ$, and phenylcarbamates, m.p. $99-100^\circ$, $80-81^\circ$, —, and $135-136^\circ$, of $CH_2Bu^{\gamma}OH$, $CMe_2Et:CH_2OH$, $CMeEt_2:CH_2OH$, and $CET_3:CH_2OH$, respectively, are described. The narcotic action of the alcohols is < that of $CBr_3:CH_2OH$. H. B.

Esters derived from heptyl alcohol. M. ROGER and F. DVOULAITZKA (Recherches, Roure-Bertrand, 1937, 79—82).—The following heptyl esters have been examined particularly with regard to their possible use in perfumery: formate, b.p. $76-77^\circ/25$ mm.; acetate, b.p. $95-96^\circ/28$ mm.; propionate, b.p. $88^\circ/10-12$ mm.; butyrate, b.p. $105^\circ/10-12$ mm.; isobutyrate (I), b.p. $98^\circ/10-12$ mm.; isovalerate, b.p. $108^\circ/10-12$ mm.; hexoate (II), b.p. $121^\circ/10-12$ mm.; heptoate, b.p. $132-133^\circ/10-12$ mm.; octoate, b.p. $145^\circ/10-12$ mm.; nonoate, b.p. $162^\circ/10-12$ mm.; decoate, b.p. $170-172^\circ/10-12$ mm.; undecoate, b.p. $167.5-168.5^\circ/3$ mm.; undecenoate (III), b.p. $174-175^\circ/10-12$ mm.; laurate, b.p. $184^\circ/10-12$ mm.; myristate, b.p. $190-191^\circ/3$ mm.; palmitate, b.p. $205-206^\circ/3$ mm.; stearate, b.p. $215-217^\circ/3$ mm., m.p. 15° ; oleate, b.p. $216-217^\circ/3$ mm.; geranate (IV), b.p. $149-151^\circ/3$ mm.; citronellate, b.p. $139-140^\circ/3$ mm.; benzoate, b.p. $150^\circ/10-12$ mm.; phenylacetate, b.p. $143^\circ/10-12$ mm.; cinnamate, b.p. $185^\circ/10-12$ mm.; anisate, b.p. $155-157^\circ/3$ mm.; *ethyl*ylate (V), b.p. $160^\circ/10-12$ mm. In the ester

series, as in that of the ethers, the same fruity, fatty and green odours, although less fugitive, accompany the heptyl radical. The odours of (I), (II), (III), (IV), and (V) appear original. H. W.

Alcohol, $C_{19}H_{40}O$, m.p. 62.5° , from oil of raspberries.—See A., III, 331.

Lipins of tubercle bacilli.—See A., III, 318.

Carbohydrates. IX. Introduction of copper into polyhydric alcohols. T. LIESER and R. EBERT (Annalen, 1937, 532, 89—94; cf. A., 1937, II, 179).—The alcohol is usually dissolved in 5—10% NH_3 and shaken with excess of $Cu(OH)_2$; after filtration, MeOH is added to the filtrate followed, if necessary, by Et_2O , whereby the complex is pptd. Alternatively, the non-reducing oligosaccharide is dissolved in aq. NEt_4OH . Complexes are thus obtained with $(CH_2OH)_2$, glycerol, erythritol, adonitol, mannitol, sorbitol, dulcitol, methylxyloside, methyl- and phenyl-glucoside, glucose, galactose, fructose, β -glucosan, maltose, lactose, cellobioside, sucrose, inositol, and tartaric acid (structures suggested). With oligosaccharides the union with Cu is less complete than with monosaccharides, probably owing to the isolated position of certain OH groups. H. W.

Triphenylmethyl ethers of glycerol and glycerol derivatives. C. D. HURD, C. O. MACK, E. M. FILACHIONE, and J. C. SOWDEN (J. Amer. Chem. Soc., 1937, 59, 1952—1954).—Glycerol α - CPh_3 ether (I) [$\beta\gamma$ - Me_2 derivative, b.p. $210-212^\circ/3$ mm., m.p. $45-50^\circ$, from (I), MeI, and Ag_2O in C_6H_6] heated at $180-190^\circ$ gives glycerol $\alpha\gamma$ - $(CPh_3)_2$ ether (II), which at 260° affords glycerol $(CPh_3)_3$ ether, m.p. $196-197^\circ$ [also prepared from glycerol (III) and CPh_3Br in C_5H_5N]. (I) is obtained from (II) and excess of (III) at $205-215^\circ$. Decomp. of the $\beta\gamma$ -dibenzoate of (I) at $260-300^\circ$ gives $CHPh_3$, $BzOH$, and an unidentified unsaturated liquid. 2:2-Dimethyl-4-triphenylmethoxymethyl-1:3-dioxolan [α -isopropylidene-glycerol CPh_3 ether], m.p. $71-73^\circ$ (from the OH-compound and CPh_3Cl in C_5H_5N), heated at $310-328^\circ$ affords $CHPh_3$, $COPh_2$, and $COMe_2$. H. B.

Characteristic reaction of yperite ($\beta\beta'$ -dichlorodiethyl sulphide). B. TELINEK (Bull. Soc. chim., 1937, [v], 4, 1813—1815).—In contact with a test paper impregnated with the $Ag-NH_3$ complex of isatin, $(CH_2Cl-CH_2)_2S$ gives a yellow spot with a green halo, which, when treated with $EtOH-AcOH$, turns deep blue. J. D. R.

Parachors of alkyl thiosulphites. H. STAMM and H. WINTZER (Ber., 1937, 70, [B], 2058—2060).—Measurements of the parachors of Me_2 , Et_2 , Pr_2 , and Bu_2 thiosulphite show the impossibility of the presence of a true, homopolar double linking, but are not sufficiently accurate to permit a decision between $(S\cdot OAlk)_2$ and $S:S(OAlk)_2$. H. W.

Preparation of alkanesulphonyl chlorides from isothiocarbamides. II. J. M. SPRAGUE and T. B. JOHNSON (J. Amer. Chem. Soc., 1937, 59, 1837—1840).—The following are prepared by the methods previously described (A., 1936, 974, 1229) unless stated otherwise: S-dodecylisothiocarbamide hydrochloride, m.p. $132-135^\circ$, and hydrobromide, m.p. $112-114^\circ$; S-hexadecylisothiocarbamide hydro-

chloride, m.p. 126—128°; S-cyclohexylisothiocarbamide hydrochloride (I), m.p. 230—231° (modified prep.), hydrobromide, m.p. 202—203°, and picrate, m.p. 173—174°; S-sec-octylisothiocarbamide picrate, m.p. 130—131°; S-tert-butylisothiocarbamide hydrochloride (II), m.p. 162° [from $\text{CS}(\text{NH}_2)_2$ and $\text{Bu}^t\text{OH}-\text{HCl}$], and picrate, m.p. 160—161°; S-iso-, m.p. 167—168°, and -sec- (III), m.p. 164.5—165.5°, butylisothiocarbamide picrates; S-p-nitrobenzyl-, m.p. 225—228°, and S- α -naphthylmethyl-, m.p. 238°, isothiocarbamide hydrochlorides; dodecane-, m.p. 42—43°, hexadecane-, m.p. 52—53°, α -methylpropane-, 89—90.5°/19 mm., α -methylheptane-, b.p. 110—111°/4 mm., cyclohexane-, b.p. 123—124°/16 mm., and p-nitrophenylmethane-, m.p. 92—93°, -sulphonyl chlorides; dodecane-, m.p. 93—94°, hexadecane-, m.p. 96.5—97.5°, cyclohexane-, m.p. 94—95°, and α -naphthylmethane-, m.p. 171—172°, -sulphonamides. Complete elimination of S as $\text{SO}_4^{''}$ occurs when (II) is treated with $\text{Cl}_2-\text{H}_2\text{O}$; partial elimination takes place with (I) and (III) (as nitrate or hydrochloride). Data previously recorded (*loc. cit.*) for $\text{Bu}^t\text{SO}_2\text{Cl}$ apply to $\text{Bu}^s\text{SO}_2\text{Cl}$. Further details are given for the prep. of EtSO_2Cl , $\text{Bu}^s\text{SO}_2\text{Cl}$, and $\text{CH}_2\text{Ph}-\text{SO}_2\text{Cl}$. H. B.

Agar. C. NEUBERG and C. H. SCHWEITZER (*Monatsh.*, 1937, 71, 46—66).—Agar is separated by cold H_2O into a sol. fraction A containing S and an insol., S-free fraction B. A is further separated by pptn. with EtOH (A_1 ; 3.6% S), with $\text{Pb}(\text{OAc})_2$ (A_2 ; 4.8% S), and with quinidine hydrochloride (A_3 ; 6% S). Agar is partly hydrolysed with 25% HBr (cold), and the Ba salt of a sol. acid with 4.3% S is isolated. The agar fraction A_3 is hydrolysed by "sulphatase" to yield H_2SO_4 and no reducing sugars, but similar hydrolysis of the HBr fission product yields both H_2SO_4 and reducing sugars. The S is present in agar in the form of polysaccharide sulphuric esters, and more of these groups are introduced by treatment with ClSO_3H in $\text{C}_5\text{H}_5\text{N}$ and CHCl_3 . J. D. R.

Partial synthesis of muscle-adenylic acid. T. JACHIMOWICZ (*Biochem. Z.*, 1937, 292, 356—359).—Phosphorylation of adenosine by Fischer's method (A., 1915, i, 296) affords a product identical (indicated by m.p., titration data, and deamination by muscle-deaminase) with muscle-adenylic acid. F. O. H.

Constitution of adenosinetriphosphoric acid. II. H. K. BARRENSCHEEN and T. JACHIMOWICZ (*Biochem. Z.*, 1937, 292, 350—355; cf. A., 1933, 1202).—The rate of deamination (Van Slyke) of the acid (I) by 30% NaNO_2 is < that of adenylic acid, whilst the rates are approx. equal with 60% NaNO_2 (cf. Lohmann, A., 1932, 1274). Bone-phosphatase (Martland and Robison, A., 1929, 603) liberates approx. $\frac{1}{3}$ of the total P of (I) as inorg. $\text{PO}_4^{''}$; this $\text{PO}_4^{''}$ originates from the difficultly hydrolysable fraction, the readily hydrolysable fraction being practically unaffected. These findings do not support Lohmann's conception (A., 1936, 53) of the constitution of (I). F. O. H.

Formation of a laevorotatory phosphoric ester from the Neuberg ester. M. G. MACFARLANE and R. ROBISON (*Enzymologia*, 1937, 4, Part II,

125—128).—Experiments are described, the results of which support the view that the varying rotations of the fructose monophosphates prepared by partial hydrolysis of hexose diphosphate are due to the formation of another laevorotatory ester, more resistant to hydrolysis than fructose 1-phosphate, from fructose 6-phosphate during heating by migration of the $\text{PO}_4^{''}$ radical to some other C atom. Samples of the laevo-ester prepared by fractional crystallisation of the brucine salts and of the Ba salts after Br oxidation had $[\alpha]_{5461}^{20}$ —24.2° and —21.3°, respectively, but these probably are not absolutely pure and still contain some fructose 6-phosphate. P. W. C.

Lysolecithin and tosylglycerides.—See A., III, 456.

Biological uptake of deuterium by fatty acids and cholesterol.—See A., III, 470.

Ester formation and structural relationships. S. G. TOOLE and F. J. SOWA (*J. Amer. Chem. Soc.*, 1937, 59, 1971—1973).—The yields of Me esters from the following acids, MeOH, and $\text{Et}_2\text{O}.\text{BF}_3$ at $64 \pm 1^\circ$ increase in the order: EtCO_2H , AcOH , $\text{CH}_2\text{Cl}.\text{CO}_2\text{H}$ (I), $\text{CHCl}_2.\text{CO}_2\text{H}$ (II), $\text{CCl}_3.\text{CO}_2\text{H}$ (III), $\text{CH}_2\text{Ph}.\text{CO}_2\text{H}$ (IV). The same order is found for (I)—(III) with MeOH-HCl and for (I)—(IV) with MeOH- H_2SO_4 . The order is reversed for (I)—(III) with EtOH-HCl and when the amides of all the above acids are treated with MeOH + BF_3 . There appears to be no direct relationship between the ionisation const. and yield of ester; the controlling factor in substituted acetic acids is probably the inductive effect of the substituent. H. B.

Preparation of [ethyl] esters [using toluene]. V. M. MITSCHOVITSCH (*Bull. Soc. chim.*, 1937, [v], 4, 1661—1669).—Aliphatic acids, or aromatic acids with CO_2H in a side-chain, heated with EtOH, PhMe, and 1—2% of H_2SO_4 give almost quant. yields of their Et esters, H_2O being eliminated in a ternary azeotropic mixture with EtOH and PhMe. Aromatic acids with nuclear CO_2H are esterified similarly, using a larger proportion of H_2SO_4 . E. W. W.

Re-esterification of carboxylic esters. I. F. ADICKES, F. PLESSMANN, and P. SCHMIDT (*Ber.*, 1937, 70, [B], 2119—2128).—The Et ester (1 mol.) is heated with anhyd. MeOH (5—10 mols.) for 8 hr. at 100° ; the mixture is fractionally distilled and tested for EtOH by the CHI_3 test. If positive, the process is repeated for a much shorter time. Et β -bromo- β -diphenylenepyrivate (I), m.p. 70—71°, is readily transformed into the Me ester (II), but the analogously constituted $\text{CBr}_3.\text{CO}.\text{CO}_2\text{Et}$, Et β -benzyl- β -diphenylenepyrivate, Et α -hydroxy- β -diphenyleneacrylate, and Et diphenyleneacetate are resistant towards EtOH. Et 2-bromo-1:3-diketohydrindene-2-carboxylate is readily transformed into the Me ester, m.p. 120—121°, and re-esterification of Et 1:3-diketohydrindene-2-carboxylate (corresponding Me ester, m.p. 132°) occurs with nearly equal readiness, whereas Et 2-chloro-1:3-diketohydrindene-2-carboxylate is unaffected. Replacement of the diketohydrindene group by a Bz residue appears to destroy activity in the cases of $\text{CBr}_2\text{Bz}.\text{CO}_2\text{Et}$, $\text{CMeBzBr}.\text{CO}_2\text{Et}$, and

CHAcBz·CO₂Et. *Et* α -bromo- α -trimethylacetylacetate is also inactive. The possibility that change is due to eliminated HBr is excluded. OH·CHMe·CO₂Et, SH·CH₂·CO₂Et, CCl₃·CO₂Et, Et₂C₂O₄, CBr₂(CO₂Et)₂, CHPh·C(CO₂Et)₂, *o*-NH₂·C₆H₄·CO₂Et, 2:4:6-(NH₂)₃C₆H₂·CO₂Et, *Et* pyridine-2-carboxylate, and *Et* α -*p*-toluenesulphonyldiphenylacetate are unchanged, but slight reaction is observed with HCO₂Et, CPh·CO₂Et, (OH)₂C(CO₂Et)₂, and CO(CO₂Et)₂. It appears, therefore, the CO α or β to CO₂Et is requisite for the ready re-esterification with MeOH, but the possible action of semiacetals as intermediates is excluded, although such compounds are readily produced. Thus crystallisation of (I) from EtOH gives the *Et* semiacetal, m.p. 113–117° (decomp.), and rapid treatment with warm MeOH yields the *Me* semiacetal, m.p. 98°. (II) gives a *Me*, m.p. 104° (decomp.), and *Et*, m.p. 102° (decomp.), semiacetal.

H. W.

Thermal decomposition of lead formate and of formic acid at a lead surface.—See A., I, 628.

One-third basic aluminium acetate solution.—See A., I, 616.

Unsaturated lower fatty acids. Crystalline derivatives. S. KOMORI and S. UENO (Bull. Chem. Soc., Japan, 1937, 12, 433–435).—"Tohaku" (*Lindera obtusifolia*) oil yields, by the ester-Br method, obtusilic acid, b.p. 148–150°/13 mm. (*p*-bromophenacyl ester, m.p. 43.3°; shown to be Δ^7 -decenoic acid by oxidation of the Me ester by KMnO₄), and linderic acid, b.p. 170–172°/13 mm., m.p. 1–1.3° (*p*-bromo-, m.p. 47.5°, and *p*-phenyl-phenacyl ester, m.p. 42.5°; *S*-benzylthiuronium salt, m.p. 139°; *Me* ester dibromide, b.p. 178–182°/2 mm.; oxidised to dihydroxylauric acid, m.p. 102°), and from the residue tsuzuic acid, m.p. 18–18.5°, b.p. 185–188°/13 mm. [*p*-phenyl-, m.p. 54.5°, and *p*-bromo-phenacyl ester, m.p. 61.3°; with O₃ gives (CH₂·CO₂H)₂].

R. S. C.

Δ^7 -Decenoic acid. Derivatives of *d*-galacturonic acid.—See A., III, 332.

Partial hydrogenation of fish oil. VIII. Constituents of [the] docosatrienoic acid produced by hydrogenating methyl clupanodonate. M. TAKANO (Bull. Chem. Soc., Japan, 1937, 12, 395–401; cf. B., 1937, 1082).—Ozonolysis of that part of the Me docosatrienoate, produced by hydrogenating clupanodonic acid (I), which gives a tetrathiocyanate indicates that the ester is a mixture of mainly $\Delta^{7\eta\delta}$ - or $\Delta^{7\eta\epsilon}$ -, some $\Delta^{7\eta\lambda}$ -, and a small amount of $\Delta^{7\eta\sigma}$ -isomeride. (I) would then be a mixture of $\Delta^{7\eta\lambda\sigma}$ - and $\Delta^{7\eta\lambda\epsilon\sigma}$ -docosapentenoic acids; the latter is probably correct (cf. Inoue and Kato, A., 1935, 195), the Δ^7 -linking being formed by shift of the Δ^{ϵ} -linking during hydrogenation. The $\Delta^{7\eta}$ -linkings, which absorb (CNS)₂, are harder to hydrogenate than the $\Delta^{\epsilon\sigma}$ -linkings, which are indifferent to (CNS)₂. R. S. C.

Electrolytic reduction of glycollic acid and lactic acid. E. BAUR (Z. Elektrochem., 1937, 43, 821–822; cf. A., 1936, 943).—At high c.d. OH·CH₂·CO₂H is reduced completely to MeOH, but with a lower c.d. HCO₂H can also be detected. It is concluded that the reaction proceeds through initial formation of MeOH and HCO₂H, the latter being

reduced subsequently to CH₂O and then MeOH. On electrolytic reduction lactic acid yields EtOH and HCO₂H in stoichiometric proportions. J. W. S.

Acetoacetic ester condensation. XI. Extent of condensation of monosubstituted acetic esters. D. C. ROBERTS and S. M. McELVAIN (J. Amer. Chem. Soc., 1937, 59, 2007–2008).—The max. yields of CH₂R·CO·CHR·CO₂Et (I) obtained (method: A., 1934, 1091) from CH₂R·CO₂Et (6 mols.) and NaOEt (1 mol.) at 95° (78° when R = H) are: R = H 75–76, Me 46–47, Et 40–42, Pr^{*a*} 34–35, Pr^{*β*} 0, Bu^{*r*} 0, Ph 53–55% (mol. ratio approx. 2:1); for R = *n*-alkyl, the extent of the condensation decreases and the time necessary for max. yields increases with the size of R. (I) are not formed from Bu^{*β*}CO₂Et and CH₂Bu^{*r*}·CO₂Et even when the reactions are carried out (cf. A., 1929, 1424) so that any EtOH formed is removed.

H. B.

Magnesium mesityl bromide as a reagent in the acetoacetic ester condensation. M. A. SPIELMAN and M. T. SCHMIDT (J. Amer. Chem. Soc., 1937, 59, 2009–2010).—Bu^{*β*}CO₂Et, CH₂Bu^{*r*}·CO₂Et, and Pr^{*β*}CO₂Et (none of which undergoes the acetoacetic ester condensation with NaOEt) are converted by Mg mesityl bromide (best added to ester) into Et α -isovalerylisovalerate (I) (51%) [use of MgPr^{*β*}Br (cf. Conant and Blatt, A., 1929, 675; Ivanov and Spasov, A., 1931, 726) gives 1.2%], Et α -*tert*-butylacetoacetate (II) (32%), b.p. 138–140°/32 mm., and Et α -isobutyrylisobutyrate (26.5%), respectively. The non-formation of these CO-esters with NaOEt is attributed to their inability to enolise; they do not give colours with FeCl₃. Et stearate is similarly converted into Et α -stearylstearate (27%), m.p. 48–49° (lit. 28–29°). (I) is hydrolysed (5% Na₂CO₃ at 225° in a steel bomb) to COBu^{*β*}. (II) is hydrolysed (aq. EtOH–KOH at 200°) to dineopentyl ketone, b.p. 185°/740 mm. (semicarbazone, m.p. 178–179°).

H. B.

Condensations brought about by bases. I. Condensation of ethyl isobutyrate to ethyl isobutyrylisobutyrate. C. R. HAUSER and W. B. RENFROW, jun. (J. Amer. Chem. Soc., 1937, 59, 1823–1826).—In accordance with a mechanism discussed for the acetoacetic ester condensation, Pr^{*β*}CO₂Et is converted by CNaPh₃ (a base sufficiently strong to form an enolate of the condensation product) in Et₂O into Et α -isobutyrylisobutyrate (I); the first stage appears to be the formation of the enolate CMe₂:C(Ö)·OEt, since treatment of this with Pr^{*β*}COCl also gives (I). Hydrolysis (aq. KOH) of (I) affords COPr^{*β*}, [semicarbazone, m.p. 160° (corr.)], also prepared from MgPr^{*β*}Br and Pr^{*β*}CN.

H. B.

Preparation and rearrangement of dialkyl maleates. P. A. SHEARER and A. M. PARDEE (Proc. S. Dakota Acad. Sci., 1935, 15, 24–26).—Rubber accelerates conversion into the corresponding fumarates; improved yields are accordingly obtained by using all-glass apparatus in the prep. CH. ABS. (r)

Reaction between esters of organic acids and magnesium isopropyl chloride. IV. Experiments with ethyl β -phenylpropionate and ethyl succinate. A. SPASSOV (Bull. Soc. chim.,

1937, [v], 4, 1658—1661).— $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and $\text{MgPr}^\beta\text{Cl}$ give C_9H_8 , and, after hydrolysis, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COPr}^\beta$ (semicarbazone, new m.p. 118—119°; cf. A., 1931, 1050). $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ similarly gives C_9H_8 , $\text{Pr}^\beta\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ (semicarbazone, m.p. 152°), and $\beta\gamma$ -dimethyloctane- $\gamma\delta$ -dione, b.p. 100—102°/9 mm. (dioxime, m.p. 173—174°). E. W. W.

Synthesis of higher dicarboxylic acids, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_{16}\cdot\text{CO}_2\text{H}$, and $\text{CO}_2\text{H}\cdot[\text{CH}_2]_{18}\cdot\text{CO}_2\text{H}$. S. SHIINA (J. Soc. Chem. Ind. Japan, 1937, 40, 324B).—By electrolysis of a solution of $\text{CO}_2\text{K}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{Et}$, the ester $\text{CO}_2\text{Et}\cdot[\text{CH}_2]_{16}\cdot\text{CO}_2\text{Et}$ (I) is obtained which by reduction is converted into $\text{OH}\cdot[\text{CH}_2]_{18}\cdot\text{OH}$. The glycol gives, through the iodide, $(\text{CH}_2)_{18}(\text{CO}_2\text{H})_2$. The following m.p. are recorded: $\text{CO}_2\text{H}\cdot[\text{CH}_2]_{16}\cdot\text{CO}_2\text{H}$, 124.2—124.6°; (I), 47.5—47.7°; $\text{CO}_2\text{Me}\cdot[\text{CH}_2]_{16}\cdot\text{CO}_2\text{Me}$, 58.9—59.2°; $\text{CO}_2\text{H}\cdot[\text{CH}_2]_{18}\cdot\text{CO}_2\text{H}$, 123.8—124.2° (Et_2 , 54.6—54.8°, and Me_2 , 65.2—65.4°, ester); $\text{OH}\cdot[\text{CH}_2]_{18}\cdot\text{OH}$, 97.5—97.8°, $\text{OH}\cdot[\text{CH}_2]_{20}\cdot\text{OH}$, 102.4—102.6°, and the corresponding iodides, m.p. 62.2—62.4° and 65.3—65.6°, respectively. F. R. S.

Condensation of acetaldehyde with ethyl malonate. A. RÖSCH (Bull. Soc. chim., 1937, [v], 4, 1643—1658).— MeCHO (I) and $\text{CH}_2(\text{CO}_2\text{Et})_2$ (II) in aq. K_2CO_3 (KCN less satisfactory) give "*Et*₂ ethanomalonate" (III), an oil [decomp. on distillation, giving (I), (II), etc.], which does not yield an Ac derivative or urethane, and is not dehydrated by H_3PO_4 . KOH hydrolyses (III) to $\text{CH}_2(\text{CO}_2\text{H})_2$; with AcCl (III) gives $\text{CEtCl}(\text{CO}_2\text{Et})_2$. E. W. W.

Catalytic hydrogenation of saturated lactones. F. WESSELY, A. MÜNSTER, and S. WANG (Monatsh., 1937, 71, 27—29).—At room temp. and pressure, hydrogenation (Pd-H_2) of β -hydroxyisopropylmalonolactone is without effect, whilst β -phenyl- β -propiolactone- α -carboxylic acid yields PhMe and $\text{CH}_2(\text{CO}_2\text{H})_2$. J. D. R.

Diazo-reaction of ascorbic acid. G. BARAC (Compt. rend. Soc. Biol., 1937, 126, 61—62).—The absorption of the diazo-colour in the visible region has been determined and the non-formation of azo-vitamin-C explained. H. G. R.

Preparation of methyl *d*-glucosonate. H. OHLE (Ber., 1937, 70, [B], 2153).—A hot solution of K diisopropylideneglucosonate (33 g.) in 10 parts by vol. of MeOH is boiled with 20 c.c. of 5N- H_2SO_4 . K_2SO_4 is filtered off and the filtrate is boiled for 3 hr. after addition of 10 c.c. of 12N-HCl. The yield of Me ester is about 90%. H. W.

Constitution of pectic substances. F. JUST (Woch. Brau., 1937, 54, 317—318).—A review of the work of Henglein, Schneider, and co-workers.

I. A. P.

Nitroguanylhya zones of aldehydes and ketones. G. B. L. SMITH and E. P. SHOUR (J. Amer. Chem. Soc., 1937, 59, 2077—2078).—Nitroguanylhya zones of the following are prepared (method: A., 1935, 769): MeCHO , m.p. 234°; PrCHO , m.p. 95°; heptaldehyde, m.p. 93°; octaldehyde, m.p. 118°; $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$, m.p. 177.5°; veratraldehyde,

m.p. 195°; hexone, m.p. 112.5°; Me *n*-amyl ketone, m.p. 109.5°; acetoacetanilide, m.p. 184°. H. B.

Kinetics of aldol condensation.—See A., I, 622.

Photolysis of *n*- and *iso*-butaldehyde.—See A., I, 627.

Addition of magnesium *n*-butyl bromide to acetone. G. PIEROTTI and T. D. STEWART (J. Amer. Chem. Soc., 1937, 59, 1773—1775).— $\text{MgBu}^\alpha\text{Br}$ and COMe_2 (slight excess) in Et_2O at 0° in complete absence of O_2 give $\text{CMe}_2\text{Bu}^\alpha\cdot\text{OH}$ (I) and smaller amounts of C_4H_8 , C_7H_{14} [from (I)], C_8H_{18} , Pr^βOH , and $(\text{CMe}_2\cdot\text{OH})_2$ (II); in presence of atm. O_2 (either during prep. of $\text{MgBu}^\alpha\text{Br}$ or during its reaction with COMe_2) $\text{Bu}^\alpha\text{OH}$ and $\text{CHMeBu}^\alpha\cdot\text{OH}$ (III) are also formed. (III) results from Et_2O peroxide which reacts as MeCHO . The ratios $\text{Pr}^\beta\text{OH}:(\text{II})$ and $(\text{I}):$ reduction products [$\text{Pr}^\beta\text{OH} + (\text{II})$] are approx. 3:1 and 6:1, respectively. H. B.

Preparation of ketones from higher fatty acids. III. Preparation of ketones from the fatty acids of hydrogenated sardine oils. IV. Preparation of ketones from the fatty acids of coconut oil and of hardened rape-seed and soya-bean oils. K. KINO (J. Soc. Chem. Ind. Japan, 1937, 40, 311B, 311—312B).—III. By heating the fatty acids with Mg, ketones of various m.p. are obtained, the acids of higher m.p. giving ketones of higher m.p.

IV. The ketones of highest m.p. are obtained from acids with high m.p. and also from acids which are least unsaturated. F. R. S.

Combination of sugars with amino-acids. II. F. LIEBEN and B. BAUMINGER. III. Experiments with animal charcoal. J. BENEK and F. LIEBEN (Biochem. Z., 1937, 292, 371—375, 376—379; cf. A., 1937, II, 401).—II. The decomp. of glucose (I) in systems containing (I) and glycine (II) in O_2 at 70° is retarded by increase in either component above the optimum ratio of (I):(II) = 1.5—2.0:1. In N_2 , the presence of (II) is still necessary for the (much lower) decomp. of (I). Presence of methylene-blue increases the decomp. almost to the aerobic val.

III. Presence of C increases the decomp. of (I) and formation of CO_2 and lactic acid; (II), however, is also decomposed with formation of CO_2 and NH_3 , a decomp. enhanced tenfold by the presence of (I).

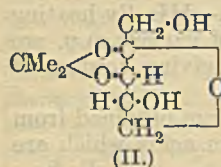
F. O. H.

Preparation of erythrose and some of its derivatives. G. E. FELTON (Iowa State Coll. J. Sci., 1935, 10, 79—81).—Ozonolysis of arabinol yields erythrose, $[\alpha]_D +11.5^\circ$ (initial), $+30.5^\circ$ (equil.), isolated as isopropylidenemethylerythroside. Acetobromoarabinose, a deoxypentose disaccharide tetra-acetate, two forms, m.p. 167—169° and 185.5°, and dihydroarabinol, b.p. 83—85°/1 mm., $[\alpha]_D \pm 48.3^\circ$, are described.

CH. ABS. (r)

Structure of monoacetone-*d*-xylulose. P. A. LEVENE and R. S. TITSON (J. Biol. Chem., 1937, 120, 607—618).—The $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$ derivative and NaI method (A., 1932, 254; 1933, 1145) is applied to 2:3:4:5-isopropylidene-fructose (I) and to isopropylidene-*d*-xylulose (II). The 1-*p*-toluenesulphonyl

derivative, m.p. 83°, $[\alpha]_D^{25} -25.9^\circ$ in EtOH, of (I) is unaffected by NaI in COMe₂ at 100°. Similarly the 1:4-di-*p*-toluenesulphonyl derivative, m.p. 71–73°, $[\alpha]_D^{25} +6.3^\circ$ in COMe₂, of (II) is not appreciably affected by NaI. This indicates that *p*-C₆H₄MeSO₂ is not attached in position 5. With MeI–Ag₂O–COMe₂, (II) gives its Me₂ derivative, b.p. 47°/0.1 mm., $[\alpha]_D^{24} -12.6^\circ$ in COMe₂, which with 0.2N-H₂C₂O₄ at 65° gives dimethylxylulose (III), m.p. 48–49°, $[\alpha]_D^{25}$ in MeOH $-26.7^\circ \rightarrow -16.3^\circ$ after 30 min. The strongly reducing properties of (III) show that the reducing group at position 2 is protected by COMe₂ in the isopropylidene derivative, but free in the Me₂ sugar. With MeOH–HCl, followed by Ag₂CO₃, (III) gives trimethyl-methylxylulose ($\alpha + \beta$), b.p. 61–64°/0.25 mm., of which three successive fractions had $[\alpha]_D^{25} -18.6^\circ$, -7.0° , and $+4.3^\circ$ in COMe₂, showing partial separation into the α - and β -forms. Further methylation (MeI–Ag₂O) gives trimethyl-methylxylulose ($\alpha + \beta$) (IV), b.p. 52°/0.25 mm., hydrolysed (H₂C₂O₄) to Me₃xylulose (V), b.p. 64°/0.25 mm., $[\alpha]_D^{25} -14.0^\circ$ in MeOH. That (IV) is 1:3:4-trimethyl-methylxylulofuranoside is shown by oxidation (HNO₃, *d* 1.42, at 59–95°), which with (IV) or (V) gives crude dimethylxylulosonic acid (VI), esterified to a mixture of the Me ester with its “methyl-



glycoside,” and some Me₂ 1-dimethoxysuccinate. By complete methylation (Purdie) and treatment with NH₃–MeOH, dimethoxysuccindiamide is obtained. This shows that (II) is 2:3-isopropylidene-*d*-xylulofuranose. With Ba(MnO₄)₂–H₂SO₄, (VI) gives a product, C₆H₁₀O₆, m.p. 151°, $[\alpha]_D^{25} -68.8^\circ$ in H₂O.

E. W. W.

Structure of β -chloralglucose. W. FREUDENBERG and A. M. VAJDA (J. Amer. Chem. Soc., 1937, 59, 1955–1957).— β -Chloralglucose [the β -glucochloralose of Coles *et al.* (A., 1929, 429)], m.p. 237.5–238°, $[\alpha]_D^{25} -17.2^\circ$ in C₆H₅N, is 1:2-trichloroethylidene-glucufuranose since it contains 3 active H (Zerevitinov), is oxidised by Pb(OAc)₄ in AcOH to CH₂O, is reduced (H₂, Ni, EtOH–NaOH) to (impure) chloroethylidene-glucufuranose, m.p. 168–170° [hydrolysed (0.5N-HCl) to glucose and CH₂Cl-CHO (2:4-dinitrophenylhydrazine, m.p. 149–151°)], and is methylated (Me₂SO₄, CCl₄, 50% NaOH) to trimethyl- β -chloralglucose (I), m.p. 113–114°, $[\alpha]_D^{25} -28.7^\circ$ in CHCl₃. Methylation (method: West and Holden, A., 1934, 636) of 1:2-isopropylidene-glucufuranose gives the 3:5:6-Me₃ derivative, b.p. 117–119°/0.7 mm., hydrolysed (aq. EtOH–HCl) to 3:5:6-trimethylglucufuranose, which with CCl₃-CHO and conc. H₂SO₄ at 10–15° affords (I) (cf. White and Hixon, A., 1933, 810).

H. B.

Reaction of 4:6-ethylidene- β -methylglucoside derivatives; 4:6-dimethylglucoside. D. J. BELL and R. L. M. SYNGE (J.C.S., 1937, 1711–1718).—4:6-Ethylidene- β -methylglucoside with N₂O₅ in CHCl₃ yields 4:6-ethylidene- β -methylglucoside 2:3-dinitrate (I), m.p. 88–89°, $[\alpha]_D^{25} -21.0^\circ$ in CHCl₃, converted by 0.1% H₂SO₄ in Ac₂O into 6-acetyl-4- α -acetoxylethyl- β -methylglucoside 2:3-dinitrate (II), m.p. 113–115°, $[\alpha]_D^{25} +22.7^\circ$ in CHCl₃, which on hydrolysis (COMe₂–HCl) yields MeCHO and unidentified products, and

on nitration (HNO₃–CHCl₃) gives MeCHO and β -methylglucose 2:3:4-trinitrate 6-acetate, m.p. 104–105°, $[\alpha]_D^{25} -27.0^\circ$ in CHCl₃, which is resistant to hydrolysis (NaOMe–CHCl₃) and to iodination (NaI–COMe₂). (II) with NaOMe in CHCl₃–MeOH yields β -methylglucoside 2:3-dinitrate, m.p. 96–98°, $[\alpha]_D^{20} -20.5^\circ$ in CHCl₃–COMe₂, acetylated (Ac₂O–NaOAc or –C₅H₅N) to β -methylglucoside 2:3-dinitrate 4:6-diacetate, m.p. 138–140°, $[\alpha]_D^{15} -5.2^\circ$ in CHCl₃, and methylated to 4:6-dimethyl- β -methylglucoside 2:3-dinitrate, m.p. 54–57°, $[\alpha]_D^{15} -13.4^\circ$ in CHCl₃, which is hydrolysed (Na₂S) to 4:6-dimethyl- β -methylglucoside (III), b.p. 130–160°/0.4 mm., m.p. 50–52°, $[\alpha]_D^{15} -28.8^\circ$ in CHCl₃ (2:3-di-*p*-toluenesulphonate (IV), m.p. 146–149°, $[\alpha]_D^{20} -14.8^\circ$ in CHCl₃). Hydrolysis of 4:6-benzylidene- β -methylglucoside 2:3-di-*p*-toluenesulphonate (H₂SO₄ or HCl in COMe₂) yields β -methylglucoside 2:3-di-*p*-toluenesulphonate (a syrup), methylated (MeI–Ag₂O) to (IV). (III) is hydrolysed (HCl) to 4:6-dimethylglucose, m.p. 156–158°, identical with the dimethylglucose, m.p. 156–157°, of Haworth and Sedgwick (A., 1926, 1228). 4:6-Ethylidene- β -methylglucoside 2:3-diacetate (V) with Ac₂O–H₂SO₄ (0.1%) yields 4- α -acetoxylethyl β -methylglucoside 2:3:6-triacetate (a syrup), which with HNO₃–CHCl₃ gives β -methylglucoside 4-nitrate 2:3:6-triacetate (VI), m.p. 112–114°, $[\alpha]_D^{25} -27.0^\circ$ in CHCl₃, reduced (Fe–Zn–AcOH) to methylglucoside 2:3:6-triacetate, which is nitrated (HNO₃–CHCl₃) to yield (VI). Nitration (HNO₃–CHCl₃) of (I) affords β -methylglucoside 2:3:4:6-tetranitrate, m.p. 116–118°, $[\alpha]_D^{15} +9.35^\circ$ in CHCl₃, whilst similar nitration of (V) yields β -methylglucoside 4:6-dinitrate 2:3-diacetate, m.p. 118–120°, $[\alpha]_D^{15} -7.3^\circ$ in CHCl₃, hydrolysed (NaOMe) to β -methylglucoside 4:6-dinitrate, m.p. 147–149°, $[\alpha]_D^{17} -5.3^\circ$ in MeOH, which is methylated (MeI–Ag₂O) to 2:3-dimethyl- β -methylglucoside 4:6-dinitrate.

J. D. R.

Calcium chloride compound of α -*d*-galactose. R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 2075).—The compound, C₆H₁₂O₆·CaCl₂·3H₂O, m.p. 129–130° (corr.), $[\alpha]_D^{20}$ (in H₂O) $+75.82^\circ$ (after 2.7 min.) $\rightarrow +42.68^\circ$, is described.

H. B.

Reduction of the methyl ester of 2:3:4-trimethyl α -methyl-*d*-galacturonide to 2:3:4-trimethyl α -methyl-*d*-galactoside. P. A. LEVENE, R. S. TIPSON, and L. C. KREIDER (Science, 1937, 86, 332–333).—Reduction has been effected in H₂ with a Cu chromite catalyst. Distillation gave a product, m.p. about 30°, $[\alpha]_D^{25} +198.4^\circ$ in H₂O, which on hydrolysis yields 2:3:4-trimethyl-*d*-galactose.

L. S. T.

Conversion of uronic acids into corresponding hexoses. I. Conversion of 2:3:4-trimethyl-methyl-*d*-galacturonide methyl ester into 2:3:4-trimethylmethyl-*d*-galactoside. P. A. LEVENE and L. C. KREIDER (J. Biol. Chem., 1937, 121, 155–164; cf. A., 1937, II, 442).—2:3:4-Trimethyl- α -methylgalacturonamide, m.p. 153–153.5°, $[\alpha]_D^{25} +121.5^\circ$ in CHCl₃ (from the Me ester and NH₃), with SOCl₂ yields the nitrite, m.p. 156–157°, $[\alpha]_D^{25} +177.6^\circ$ in CHCl₃. The CN group of this could not be eliminated. AgNO₃ in aq. NH₃–MeOH followed by H₂S gave only the thioamide, m.p. 182–183°

(also prepared from the nitrile and H_2S in $\text{MeOH-NH}_4\text{OH}$); heating with conc. aq. NH_3 gave the amide, whilst $\text{Na} + \text{MeOH}$ gave a compound, probably the Me iminogalacturonate, m.p. $65-65.5^\circ$, $[\alpha]_D^{25} +19.4^\circ$ in CHCl_3 . The nitrile is reduced (Raney's catalyst) to 6-amino-2:3:4-trimethyl- α -methyl-d-galactoside, b.p. $172^\circ/25 \text{ mm.}$, $[\alpha]_D^{25} +161.3^\circ$ in CHCl_3 , which with HNO_2 gives 2:3:4-trimethyl- α -methyl-d-galactoside, $[\alpha]_D^{25} +132.2^\circ$ in MeOH . A. Li.

***l*-Sorbitose. II. New acetyl and methyl derivatives of *l*-sorbitose. Numerical relationships in the *l*-sorbitose series.** H. H. SCHLUBACH and G. GRAEFE (Annalen, 1937, 532, 211-227; cf. A., 1933, 1145).—*l*-Sorbitose with Ac_2O in well-cooled $\text{C}_6\text{H}_5\text{N}$ gives α -*l*-sorbitose tetra-acetate (I), m.p. 100.8° (corr.), $[\alpha]_D^{20} -21.3^\circ$ in CHCl_3 , converted by Ac_2O and NaOAc at 100° into α -sorbitose penta-acetate (II), m.p. 97.0° , $[\alpha]_D^{20} -56.5^\circ$ in CHCl_3 . (I) with PCl_5 - AlCl_3 or with PCl_5 alone gives very unstable, partly halogenated products, whereas with anhyd. HCl at 0° α -acetochlorosorbitose (III), m.p. 67.0° , $[\alpha]_D^{20} -83.3^\circ$ in CHCl_3 , is obtained in 72% yield; it is still less stable than the corresponding fructose compound, but can be preserved for a few weeks in abs. Et_2O at 0° . It is re-converted by AgNO_3 into (I). Treatment of (III) with AgOAc in boiling C_6H_6 does not lead to complete replacement of Cl , but in Ac_2O at 80° 1 - β -sorbitose penta-acetate (IV), m.p. 113.8° , $[\alpha]_D^{20} +74.4^\circ$ in CHCl_3 , is obtained, a Walden inversion occurring as with the aldohalogenoses, but not with β -acetochlorofructose. Treatment of (III) with AgNO_3 and Ag_2CO_3 in MeOH yields β -methylsorbitoside tetra-acetate, m.p. 75.0° , $[\alpha]_D^{20} +79.8^\circ$ in CHCl_3 . The isomeric α -methylsorbitoside tetra-acetate has m.p. 89.5° , $[\alpha]_D^{20} -52.6^\circ$ in CHCl_3 . β -Methylsorbitoside (V), has m.p. 106.2° , $[\alpha]_D^{20} +39.0^\circ$ in H_2O , $+84.3^\circ$ in MeOH , $+97.1^\circ$ in EtOH , $+101.4^\circ$ in EtOAc . Hydrolysis of (V), α -methylsorbitoside (VI), and β -methylfructoside, in contrast to that of the Me glucosides of the aldohexoses, occurs rapidly at 20° , and since they are all pyranose derivatives, the difference must be ascribed to that usually observed between a *sec.* and a *tert.* OH. The aldofuranosides are readily hydrolysed. The half-periods of inulin and sucrose are of the same order of magnitude as those of (V) and (VI). Generally, the differences in the rates of hydrolysis of ketopyranoses and ketofuranoses are not so great as those between the corresponding aldose compounds. The vals. of $[\alpha]_D$ for (II) and (IV) and (V) and (VI) enable the validity of Hudson's rules to be tested for ketoses on an extended basis. The observation that the increments for the different groups in the case of fructose are generally appreciably $>$ those for similar groups in the aldose series cannot be generalised, since the α -vals. of *l*-sorbitose are invariably considerably $<$ those of *d*-fructose and vary irregularly around those of the aldoses. The only general differences between ketoses and aldoses are the greater reactivity of the former and the more pronounced tendency to form derivatives of the keto-form. Comparison of (V) and (VI) with the methylfructosides shows close resemblance between (V) and α - and (VI) and β -methylfructoside. The assignment of sorbitose to the *l*-series and the designation of its derivatives

therefrom in consonance with Hudson's rules are inappropriate. H. W.

Ring structure of α -methyl-*l*-sorbitoside. R. L. WHISTLER and R. M. HIXON (J. Amer. Chem. Soc., 1937, 59, 2047-2048; cf. Arragon, A., 1936, 1234).— α -Methyl-*l*-sorbitoside (I) (tetra-acetate, m.p. 88° , $[\alpha]_D^{25} -52.4^\circ$ in CHCl_3 , unaffected by AcCl-HCl) is methylated (Me_2SO_4 followed by $\text{MeI-Ag}_2\text{O}$) to the Me derivative (II), $[\alpha]_D^{25} -48.8^\circ$ in CHCl_3 , hydrolysed (2% HCl) to tetramethyl-*l*-sorbitose (III), $[\alpha]_D^{25} -10.2^\circ$ in CHCl_3 , $+4.95^\circ$ in MeOH . Oxidation [HNO_3 (d 1.42) at $70-95^\circ$] of (III) gives *d*-dimethoxysuccinic acid, indicating that (I)-(III) possess pyranoid structures. H. B.

Fructose anhydrides. XXI. Synthetic difructose anhydrides. H. H. SCHLUBACH and H. KNOOR (Annalen, 1937, 532, 207-210).—Repetition of the work of Schlubach and Elsner (A., 1929, 51) leads to the isolation of a hygroscopic, amorphous compound which does not reduce Fehling's solution. Its COMe_2 content (1.4%) and its properties in conjunction with the results of acetylation and methylation indicate that it is the difructose anhydride (I) obtained by Schlubach and Behre (A., 1934, 174) by the action of HCl on fructose, contaminated with a dextrorotatory, probably isopropylidene compound. A second substance (II) had $[\alpha]_D +44^\circ$ in H_2O , $+52^\circ$ in MeOH , but higher vals. are occasionally observed. Its reducing power increases with the time of experiment and hence is due to causes other than the presence of reducing groups. It is slowly hydrolysed by $\text{N-H}_2\text{SO}_4$. When methylated it gives a *Me ether* ($\text{OMe} = 45.3\%$), b.p. $141^\circ/0.05 \text{ mm.}$, $[\alpha]_D^{20} +55.1^\circ$ in H_2O , $+49.8^\circ$ in CHCl_3 , $+47.8^\circ$ in C_6H_6 , $+40.4^\circ$ in CCl_4 , hydrolysed to a trimethylfructose, b.p. $93^\circ/0.05 \text{ mm.}$, $[\alpha]_D^{20} +22.2^\circ$ in H_2O , $+15.5^\circ$ in CHCl_3 , $\pm 0^\circ$ in C_6H_6 , -7.3° in CCl_4 , which gives a non-cryst. phenylosazone. (II) appears therefore to be a difructose anhydride and unlike (I) to be a fructofuranose. The mol. wt. follows from the b.p. of the Me derivative. The simultaneous production of both types of anhydride is understandable since in solutions of fructose the furanose form is present in considerable proportion with the pyranose variety. From these forms under the influence of acids very varied difructose anhydrides result all of which are hydrolysed with great difficulty by acids and are very stable, saturated systems which show no tendency to polymerise. H. W.

aldehydo-Derivatives of *d*- α -galaheptose. R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 1898-1900).—*d*- α -Galaheptose [oxime (I), m.p. 179° (decomp.) (all m.p. except this are corr.), $[\alpha]_D^{20}$ (in H_2O) $-5^\circ \rightarrow -1.6^\circ$] (as hydrate) and EtSH in conc. HCl give *d*- α -galaheptose *Et mercaptal*, m.p. $204-205^\circ$, $[\alpha]_D^{20} -9.7^\circ$ in $\text{C}_6\text{H}_5\text{N}$, the hexa-acetate, m.p. $145-146^\circ$, $[\alpha]_D^{20} +5.6^\circ$ in CHCl_3 , of which with $\text{HgCl}_2 + \text{CdCO}_3$ in COMe_2 affords aldehydo-*d*- α -galaheptose hexa-acetate (II), m.p. $173-174^\circ$, $[\alpha]_D^{20} +27^\circ$ in CHCl_3 [oxime (III), m.p. 130° , $[\alpha]_D^{20} +16.3^\circ$ in CHCl_3], acetylated further ($\text{Ac}_2\text{O-AcOH}$ -conc. H_2SO_4 at 20°) to the octa-acetate, m.p. 112° , $[\alpha]_D^{20} +19.8^\circ$ in CHCl_3 . Acetylation (Ac_2O , $\text{C}_6\text{H}_5\text{N}$) of (I) or (III) affords aldehydo-*d*- α -galaheptoseoxime

hepta-acetate, m.p. 125—126°, $[\alpha]_D^{20} +38.6^\circ$ in CHCl_3 , which when heated to 170° passes into *d-α-galaheptonitrile hexa-acetate*, m.p. 194°, $[\alpha]_D^{20} +31.7^\circ$ in CHCl_3 , also formed from (I) or (III) and $\text{Ac}_2\text{O}-\text{NaOAc}$. *d-α-Galaheptosesemicarbazone*, m.p. 136—137° $[\alpha]_D^{20}$ (in H_2O) $-22^\circ \rightarrow +32.9^\circ$, is acetylated (Ac_2O , $\text{C}_5\text{H}_5\text{N}$) to the *semicarbazone*, m.p. 180°, $[\alpha]_D^{20} +16.7^\circ$ in CHCl_3 , of (II). There is no parallelism between the rotations of the above compounds and those of the corresponding derivatives of mannose. H. B.

Behaviour of glucosides when micro-sublimed. R. FISCHER (Arch. Pharm., 1937, 275, 516—526).—Micro-sublimation of *æsculin*, *fraxin*, *daphnin*, *phloridizin*, *quercitrin*, *baptisin*, *arbutin*, *solanin*, *digitonin*, *hederin*, and other saponins gives the aglucones, but *syringin* and *salicin* sublime unchanged. The aglucone is best obtained by moistening with HCl before sublimation; this allows identification of the glucosides in and characterisation of many natural products. *Solanidine hydrochloride* sublimes. R. S. C.

Strophanthin. J. KRAUS (Naturwiss., 1937, 25, 651).—From a technical strophanthin prep. after mild hydrolysis, a trisaccharide, *glucosidoglucosidocymarose*, $\text{C}_{19}\text{H}_{34}\text{O}_{14}$, m.p. 217—220°, has been isolated; it is not identical with the methylstrophanthobioside of Feist (A., 1898, i, 329). From the same strophanthin prep. after acetylation an *acetylstrophanthin*, m.p. 216—220°, was obtained. W. O. K.

Scoparin.—See A., III, 333.

Fructosides of Amaryllidaceæ. *Lycoris* and *Narcissus*.—See A., III, 503.

Fructose anhydrides. XX. Constitution of asphodelin. H. H. SCHLUBACH and H. LENDZIAN (Annalen, 1937, 532, 200—207).—Extraction of *Asphodelus* tubers (harvested in October) with H_2O , removal of proteins by basic Pb acetate, and pptn. with EtOH gives the crude carbohydrate, which is further purified by repeated fractional pptn. by EtOH from H_2O . The persistent presence of N in small amount shows that homogeneity is not reached by this method. The product is therefore acetylated in $\text{C}_5\text{H}_5\text{N}$ and the *acetate* (I), $[\alpha]_D^{20} -16.6^\circ$ in CHCl_3 , after repeated pptn. from C_6H_6 by light petroleum is deacetylated (Zemplén) to asphodelin (II), $[\alpha]_D^{20} -30.9^\circ$ in H_2O . For a polyfructosan it is remarkably stable to heat. The reducing val. (Bertrand) is 0.35%, the aldose val. 0.4%. During hydrolysis the aldose val. increases to 11.1%. Methylation of (I) in COMe_2 affords *methylasphodelin*, $[\alpha]_D^{20} -33.3^\circ$ in C_6H_6 , which on hydrolysis gives 1:3:4:6-tetramethylfructose, a mixture of trimethylfructose and -glucose, and a dimethylfructose, $[\alpha]_D^{20} +19.6^\circ$ in CHCl_3 , apparently identical with that derived from methylirisin and methylgraminin. The ratio of the amounts of tetra-, tri-, and di-methylhexoses, calc. as fructose, is nearly 1:5:1. (II) must therefore contain at least six hexose residues; this is roughly confirmed by cryoscopic determinations of the mol. wt. The aldose val. of the trimethylhexose fractions points to the presence of at least one glucose unit in five hexose units. Whether the glucose is an integral component of (II) or the product of the fission of an accompanying glucose anhydride remains undecided.

The latter possibility is supported by the behaviour of the material obtained from tubers collected in January. The type of structure of (II) resembles that of sinistrin. H. W.

Fructose anhydrides. XIX. Constitution of asparagosin. H. H. SCHLUBACH and H. BÖE (Annalen, 1937, 532, 191—200).—The fresh asparagus roots are extracted with H_2O , proteins are removed with basic Pb acetate, and the crude carbohydrate is purified by systematic fractional pptn. by EtOH from H_2O . Thus obtained, *asparagosin* (I) has m.p. 197—198° after softening at 170° and swelling at 193°, $[\alpha]_D^{20} -32.4^\circ$. It is acetylated in $\text{C}_5\text{H}_5\text{N}-\text{H}_2\text{O}$ to an Ac_2 derivative, which in anhyd. $\text{C}_5\text{H}_5\text{N}$ passes into the *triacetate* (II), m.p. 93° after softening at 80°, $[\alpha]_D^{20} -20.1^\circ$ in CHCl_3 , which when deacetylated (Zemplén) affords (I) with $[\alpha]_D^{20} -32.6^\circ$ in H_2O . It does not react with Fehling's solution. The mol. wt., determined cryoscopically in H_2O , corresponds with the presence of 9—10 fructose units. Acid hydrolysis causes 92.2% fission as a max. (measured by the reducing val. according to Bertrand). According to the method of Auerbach and Bodländer aldoses are absent so that (I) is composed entirely of fructose units. Treatment of (II) with Me_2SO_4 and alkali followed by $\text{MeI}-\text{Ag}_2\text{O}$ gives *trimethylasparagosin*, $[\alpha]_D^{20} -47.8^\circ$ in CHCl_3 . This is hydrolysed by alcoholic $\text{H}_2\text{C}_2\text{O}_4$ followed by 0.25% HCl to a tetramethylfructose, $[\alpha]_D^{20} +21.1^\circ$ to $+15.3^\circ$ in CHCl_3 , 3:4:6-trimethylfructose, $[\alpha]_D^{20} +26.1^\circ$ to $+23.0^\circ$ in CHCl_3 (phenylosazone, forms, m.p. 126—127° and 78—79°, respectively), identical with that derived from inulin, and a dimethylfructose, $[\alpha]_D^{20} +14.0^\circ$ to $+21.0^\circ$ in CHCl_3 , identical with that derived from irisin and graminin (III). The ratio of the amounts of these products, calc. as fructose, is almost exactly 1:8:1. (I) is therefore a polyfructosan ($\text{C}_6\text{H}_{10}\text{O}_5$)₁₀. In its special structure it is allied most closely to inulin, of which it may be regarded as a model to scale 1:3. Since the presence of an open chain in (I) is impossible and that of a large ring must be assumed for the same reasons as in the cases of (III), sinistrin, and triticin the existence of (I) is a further argument for the presence of a large ring in inulin. H. W.

Constitution of galactogen. I. H. H. SCHLUBACH and W. LOOP [with H. SCHMIDT] (Annalen, 1937, 532, 228—235).—Galactogen (I) is separated as the Cu compound from its mixture with glycogen (II) in the vineyard snail (cf. May, A., 1934, 1251) and, after regeneration, is treated with malt diastase until further action does not occur. It has then $[\alpha]_D^{20} -17.6^\circ$ in H_2O . The half-period of acid hydrolysis of (I) is somewhat < that of (II). May's explanation that the difference in the galactose (III) content of the hydrolysate according as it is calc. from the reducing power or optical activity is due to a peculiar variety of (III) is unnecessary; the phenomenon is probably due to varying amounts of reversion products depending on the conditions of reaction. Direct methylation of (I) by KOH and Me_2SO_4 is difficult. It is therefore treated with aq. $\text{C}_5\text{H}_5\text{N}$ and Ac_2O followed by anhyd. $\text{C}_5\text{H}_5\text{N}$ and Ac_2O and the *acetate* is treated with $\text{Me}_2\text{SO}_4-\text{KOH}$ in COMe_2 , then with Na and MeI in liquid NH_3 -anisole, and finally with $\text{Ag}_2\text{O}-\text{MeI}$,

thereby yielding *methylgalactogen* (44.7% OMe; calc. 45.6%), $[\alpha]_D^{20} -71.1^\circ$ in CHCl_3 . This is hydrolysed completely by 40% HCl to a mixture of tetramethyl- and dimethyl-methylgalactosides without apparent formation of trimethyl-methylgalactoside. The components are therefore present in the ratio 1:1. The structure of (I) resembles therefore that of irisin and differs completely from that of (II) which gives mainly a trimethylglucose when hydrolysed. H. W.

So-called "soluble starch." W. S. REICH and P. TRPINAC (Bull. Soc. chim., 1937, [v], 4, 1921—1923).—"Sol starch," prepared from potato starch by hydrolysis with glycerol at 220° , is benzoylated ($\text{BzCl}-\text{C}_6\text{H}_5\text{N}$) to a *tribenzoate* of "amylone" (a non-reducing sugar with 3 free OH per glucose unit), and a different *tribenzoate*, $[\alpha]_D^{25} +64.7^\circ$ in CHCl_3 . By prolonging the time, or increasing the temp. of hydrolysis of the starch, a non-reducing sugar with 4 free OH per glucose unit is formed (*octabenzooate*, $[\alpha]_D^{25} +70.6^\circ$ in CHCl_3). J. D. R.

Hydrolysis of starch paste by β -amylase and by heating under pressure.—See A., III, 430.

Application of cleavage type of oxidation by periodic acid to starch and cellulose. E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1937, 59, 2049—2050).—Maize starch (I) is oxidised by aq. HIO_4 (1 mol. consumed per $\text{C}_6\text{H}_{10}\text{O}_5$ during 24 hr.) at $21-22^\circ$ to a product, $[\alpha]_D^{20} +9^\circ$ in H_2O , which reduces Fehling's solution, gives an immediate ppt. with $\text{NHPh}\cdot\text{NH}_2$, and shows no colour with I. Similar products, $[\alpha]_D^{20}$ (in H_2O) -25° and -29° , respectively, are formed [more slowly than from (I)] from cotton and filter-paper; the amount of HIO_4 consumed is >1 mol. probably owing to further oxidation during prolonged contact. Hydrolysis (0.1N-HCl at $99-100^\circ$) of all the products gives (—)-solutions having approx. the equilibrium val. for *d*-erythrose. H. B.

Carbohydrates. X. Viscosity of solutions of cellulose. T. LIESER and R. EBERT (Annalen, 1937, 532, 94—103; cf. A., 1937, II, 179).—In agreement with Staudinger the sp. viscosity of solutions of cellulose (I) in $\text{NH}_3\text{-Cu}(\text{OH})_2$ is found to be independent of temp. and concn. η_{sp} of the same sample of (I) dissolved in $\text{NET}_4\cdot\text{OH}$ and diluted with 0.7N-NaOH is about thrice as great and dependent on temp. and concn. Similar results are obtained in $\text{NET}_4\cdot\text{OH}$ alone, in NMe_3 , *p*-cresol diluted with NaOH, and in $\text{PET}_4\cdot\text{OH}$ diluted with NaOH. The state of dissolution of (I) is not regarded as essentially different in the two sets of experiments; this view is supported by the observation that η_{sp} of (I) in $(\text{CH}_2\cdot\text{NH}_2)_2$ is similar to that in org. bases. It appears impossible to regard the interaction of (I) and $\text{Cu}(\text{OH})_2\text{-NH}_3$ otherwise than as a pseudostoichiometric, micellary surface change regulated by the ratio, micelle surface:micelle content. This ratio appears to be true also in the cases of mercerisation, xanthate reaction, addition of HClO_4 , and production of the primary Knecht compound. Permutoid introduction of Cu into (I) dissolved in strong org. bases is possible if the temp. is kept sufficiently low. The dissolution of (I) in such bases of sufficiently high mol. wt. and concn. occurs since they force apart the main valency

chains at the surface of the micelle, conquering the micellary forces until they penetrate to the thread mols. situated within the micelles; these become solvatised with production of mol. compounds. Low temp. favour the production of these as of all mol. compounds, whereas at higher temp. they become dissociated. Apart from hydrolytic influences, similar conditions maintain in solutions of (I) in conc. inorg. acids. These agents have a unique position as solvents of (I). Mild solvents, e.g., Schweitzer's solution, are incapable of overcoming the micellary forces of highly polymerised (I). The differences of η_{sp} in org. bases or inorg. acids and in $\text{Cu}(\text{OH})_2\text{-NH}_3$ lead to the hypothesis that, other things being equal, micellary and mol. solutions of (I) have nearly the same sp. η . It is therefore impossible to distinguish by measurements of viscosity between the micellary and mol. condition. H. W.

Highly polymerised compounds. CLXXV. K_m constants of cellulose acetates. H. STAUDINGER and A. E. WERNER (Ber., 1937, 70, [B], 2140—2148).—In consequence of the gradual alteration of K_m in cellulose derivatives of lower mol. wt. the viscosity of dil. solutions of tetra-acetylglucose laurate and stearate, *ditetra-acetylglucose adipate*, m.p. $163-5^\circ$, *dihepta-acetylcellobiose adipate*, m.p. $225-226^\circ$, and *sebacate*, m.p. $234-235^\circ$, has been determined. After making allowance for the viscosity of the aliphatic chain K_m for the glucose acetate residue shows a progression. In explanation it is assumed that the ratio of diameter to length of mol. must be very high for exact fulfilment of the laws of η . With short-chained, irregularly formed mols. a group which increases the diameter at any point causes increase in η . The simpler glucose derivatives have unbranched, extended thread mols. Since the K_m consts. of cellulose acetates can be calc. from those of these products, it follows that the macromols. of meso- and eu-colloidal cellulose acetates and of cellulose itself must be constructed of long, unbranched glucose chains. The mols. of starch are extended but branched, whereas glycogen and its derivatives are composed of spherical mols. The K_m consts. of *cetyl triacetylglallate*, m.p. 88° , and *ditriacetylgalloyloxy-decane*, m.p. $122.5-123^\circ$, in COMe_2 , CHCl_3 , and dioxan are almost identical with those of the corresponding glucose triacetate derivatives. For glucose penta-benzoate and penta-acetate and maltose octa-acetate η_{sp}/c is const. over a large region of concn. as expected for compounds with spherical mols. H. W.

[Reaction of] monochloroamine with organolithium and -zinc compounds. G. H. COLEMAN, J. L. HERMANSON, and H. L. JOHNSON (J. Amer. Chem. Soc., 1937, 59, 1896—1897).— NH_2Cl and ZnR_2 ($\text{R} = \text{Et}, \text{Pr}^a$) in Et_2O -light petroleum at -30° give NH_2R (46—57%) and NH_3 (41—47%); NH_2R (8—17%), NHR_2 (5—8%), NH_3 (27—38%), and N_2 are formed using NCl_3 . LiR ($\text{R} = \text{Me}, \text{Bu}^a, \text{Ph}, p\text{-tolyl}$) added to NH_2Cl at about -50° gives max. yields (33—39%) of NH_2R ; NH_3 is also formed. H. B.

Addition of butylamine to butyl isocyanide. T. L. DAVIS and W. E. YELLAND (J. Amer. Chem. Soc., 1937, 59, 1998—1999).— Bu^a isocyanide (I),

b.p. 124—125°/761.5 mm. (from Bu^aI and AgCN at 125—130°), with NH₂Bu^a and ZnCl₂ at 105—110° gives 18.4% of *NN'*-di-*n*-butylformamidine (II) [picrate, m.p. 114.5—116.5°, which when heated > m.p. or fused with NaOH affords (I)]. (II) is also produced [with (I) and tarry products] from NH₂Bu and CHCl₃ (or CHBr₃), preferably in presence of ZnCl₂. (II) is also synthesised from HCO·NHBu^a, b.p. 124—126°, NH₂Bu^a, HCl, and POCl₃. H. B.

Compounds of carbonyl chloride with hexamethylenetetramine, *m*-toluidine, and ethylenediamine. N. A. PUSHIN and R. V. MITTÉ (Annalen, 1937, 532, 300—301).—Even when an excess of COCl₂ in CHCl₃ is employed, the compound COCl₂·2C₆H₁₂N₄ is obtained from (CH₂)₆N₄. COCl₂ and *m*-C₆H₄Me·NH₂ afford *di-m*-tolylcarbamide hydrochloride, m.p. 162°. *Ethylenecarbamide hydrochloride*, CO<NH·CH₂, HCl, is derived from (CH₂·NH₂)₂.

H. B.

Onium compounds. XVII. Thioethers of formocholine and their sulphones. R. R. RENSHAW and D. E. SEARLE (J. Amer. Chem. Soc., 1937, 59, 2056—2058).—SALK·CH₂·NMe₂ (from NHMe₂, 40% CH₂O, and AlkSH) with MeI in PhMe afford *trimethyl(alkylthiomethyl)ammonium iodides*, of which the following are described: Alk = Me, m.p. 136—137°, Et, m.p. 119—120°, Pr^a, m.p. 111—113°, Pr^β, m.p. 143—145°, Bu^a, m.p. 123—126°, Bu^β, m.p. 153—154°. The corresponding sulphates are oxidised (5% KMnO₄ in neutral solution) to *trimethyl(alkanesulphonylmethyl)ammonium sulphates*, [AlkSO₂·CH₂·NMe₂]₂SO₄; the following are described: Alk = Et, decomp. 178°, Pr^a, decomp. 190°, Pr^β, decomp. 190°, Bu^a, decomp. 190°, Bu^β, decomp. 197°. The following *triethyl(alkylthiomethyl)ammonium iodides* are similarly prepared from SALK·CH₂·NEt₂ and EtI: Alk = Me, m.p. 134—136°, Et, m.p. 102—103.5°, Pr^a, m.p. 81—85°, Pr^β, m.p. 132—133°, Bu^β, m.p. 100—101°. M.p. are corr. Pharmacological properties are discussed (cf. A., 1932, 540). H. B.

Acetylcarnitine. R. KRIMBERG and V. VITANTS (Acta Univ. Latviensis, Med. Fak. Ser., 1933, 1, 297—303).—Carnitine and AcCl yield *acetylcarnitine chloride*, m.p. 181°, [α]_D²⁰ −26.91°, which, with moist Ag₂O, yields *acetylcarnitine*, m.p. 145°, [α]_D²⁰ −19.52° (Au, m.p. 128°, and Pt, m.p. 187°, salts); this with Ba(MnO₄)₂ gives the same acetobetaine as does carnitine, thus showing that the OH is in the β-position. CH. ABS. (r)

Preparation of the simpler α-alkylaminoacids. I, II. W. COCKER (J.C.S., 1937, 1693—1695, 1695—1696).—I. An improved prep. of sarcosine (I) (cf. A., 1931, 1402) is described. Interaction of PhSO₂·NH·CH₂·CO₂H with EtI and NaOH, followed by hydrolysis (H₂SO₄), yields NH₂Et·CH₂·CO₂H (II), m.p. 180—182° [lit. 160° (decomp.)] (*phenylhydantoin*, m.p. 110°). *N*-Propylglycine, m.p. 196—198° (Bz derivative, m.p. 89—90°), is similarly formed using PrI. *N*-Benzenesulphonylalanine is methylated (Me₂SO₄) to *N*-benzenesulphonyl-*N*-methylalanine, m.p. 96—97°, hydrolysed (H₂SO₄) to *N*-methylalanine, m.p. 315—317° (decomp.) [lit. 260° (decomp.)] (Bz derivative, m.p. 129—129.5°; *phenylhydantoin*,

m.p. 145—146°). Hydrolysis of *N*-benzenesulphonyl-*N*-benzylglycine with H₂SO₄ yields glycine (III), and with conc. HI, CH₃PhI and PhSH.

II. 2 : 1-OMe·C₁₀H₇·SO₂Cl and (III) in C₆H₆·NaOH afford *N*-2-methoxynaphthalene-1-sulphonylglycine, m.p. 184.5°, methylated (Me₂SO₄) to *N*-2-methoxynaphthalene-1-sulphonylsarcosine, m.p. 145°, hydrolysed (60% H₂SO₄) to β-C₁₀H₇·OMe and a little (I). Similarly, *mesitylenesulphonylglycine*, m.p. 154.5°, is prepared from *mesitylenesulphonyl chloride* and (III) is methylated (Me₂SO₄) to *mesitylenesulphonylsarcosine*, m.p. 164—165°, and hydrolysed (60% H₂SO₄) to (I). *m*-Xylene-4-sulphonyl chloride and (III) yield *N*-*m*-xylene-4-sulphonylglycine (IV) (*hydrate*, m.p. 76°; *anhyd.*, m.p. 110—110.5°), methylated (Me₂SO₄) to *N*-*m*-xylene-4-sulphonylsarcosine, m.p. 104.5—105°, also hydrolysed by H₂SO₄ to (I). (IV) heated with *p*-C₆H₄Me·SO₃Et and NaOH yields *N*-*m*-xylene-4-sulphonyl-*N*-ethylglycine, m.p. 108—109°, hydrolysed by H₂SO₄ to (II). J. D. R.

Infra-red absorption spectra of the stereoisomerides of cystine. N. WRIGHT (J. Biol. Chem., 1937, 120, 641—646).—Determination of the infra-red absorption spectra of *l*-, *d*-, *dl*-, and *meso*-cystine shows that *dl*-cystine obtained by crystallisation is a compound. (I) from protein and cystinuric urine have identical spectra. A. L.

Multivalent amino-acids and peptides. IX. Synthesis of *l*-cystinyl-*l*-cystine. J. P. GREENSTEIN (J. Biol. Chem., 1937, 121, 9—17).—1-Cysteinyl-*l*-cysteine hydrochloride, m.p. 166°, [α]_D²² +35° in 0.2N-HCl [from anhydrocysteinylcysteine (A., 1937, II, 262) with cold conc. HCl for 4 days], is oxidised by air in aq. NH₃ at *p*_H 8.5 to *l*-cystinyl-*l*-cystine (I), [α]_D²² −60° in *n*-HCl (*dihydrochloride*), hydrolysed by dil. HCl to cystine having the same [α] as the initial material. The mol. wt. of (I) and of the Me₂ ester, m.p. 257° (decomp.), of its NN'-Bz₂ derivative, m.p. 220° (decomp.), indicate the formula [S·CH₂·CH(NH₂)·CO·NH·CH(CO₂H)·CH₂·S]₂. A. Li.

Synthesis of substances related to capsaicin. P. C. MITTER and S. C. RAY (J. Indian Chem. Soc., 1937, 14, 421—424).—The following isobutylamides, in order of decreasing pungency, are described: Δ^a-hepteno-, b.p. 140°/4 mm., Δ^a-noneno-, b.p. 170°/7 mm., *n*-hepto-, b.p. 130°/7 mm., benzo-, *cinnamo*-, m.p. 114°, *n*-hexo-, b.p. 136°/9 mm., Δ^a-hexeno-, b.p. 138°/4 mm., *n*-octo-, b.p. 155°/8 mm., Δ^a-octeno-, b.p. 150°/4 mm., Δ^β-deceno-, b.p. 155°/4 mm., Δ^ω-undeceno-, b.p. 175°/5 mm., *aniso*-, m.p. 105—106°. A. Li.

Stability and toxicity of a complex salt of silver chloride and thiocarbamide. W. M. LAUTER and A. M. STAUFF (J. Amer. Pharm. Assoc., 1937, 26, 724—726).—The complex AgCl₅CS(NH₂)₂ is unstable in H₂O, AgCl₂CS(NH₂)₂ being formed. AgCl₇CS(NH₂)₂ is stable in H₂O and has a toxicity of approx. 0.3 mg. per g. in rats. F. O. H.

Carbamide series. XIV. Structure of the guanidonium ion; evidence from electrolysis. T. L. DAVIS, W. E. YELLAND, and C. C. MA (J. Amer. Chem. Soc., 1937, 59, 1993—1997).—Dil. NH₄ amalgams appear to be formed when guanidine salts

are electrolysed in H_2O or org. solvents using a Hg cathode. Evidence is discussed to show that the guanidonium ion is $^+\text{C}(\text{NH}_2)_3$; electrolysis results in the production of $[\text{C}(\text{NH}_2)_3]_2$, which decomposes to NH_3 and $(\text{CN})_2$ [subsequently reacting with part of the NH_3 to give NH_4CN and $\text{CO}(\text{NH}_2)_2$ (via NH_4CNO)].

H. B.

Reduction of nitroguanidine. IX. Reduction of nitrosoguanidine to aminoguanidine. E. LIEBER and G. B. L. SMITH (J. Amer. Chem. Soc., 1937, 59, 1834—1835).—Aminoguanidine (I) is best prepared from nitrosoguanidine (II) by reduction with H_2 and Raney Ni in MeOH at 25° . The effects of catalyst, temp., and solvent are investigated. The yields of (I) from (II) are generally $>$ those from nitroguanidine (cf. A., 1937, II, 10), except for PtO_2 in 15% AcOH [in which solvent (II) is unstable].

H. B.

Cacodylates of zinc. R. THIOLLAIS and H. PERDREAU (Bull. Soc. chim., 1937, [vi], 4, 1896—1898).— ZnO and $\text{AsMe}_2\text{O}_2\text{H}$ yield *Zn cacodylate monohydrate* and *heptahydrate*, also obtained from ZnSO_4 and Ba cacodylate.

J. D. R.

Complex compounds of mercury halides with the halides of the aliphatic amines.—See A., I, 628.

Ring fission in complex platinum compounds.—See A., I, 630.

Ethylene compounds of platinum.—See A., I, 630.

Dipole moment of *n*-propylcyclopropane.—See A., I, 499.

Synthesis of cyclopentanespirocyclopentane. N. CHATTERJEE (Sci. and Cult., 1936, 1, 478).—Et 1-cyanocyclopentane-1-cyanoacetate (from cyclopentanone cyanohydrin and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$) with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ gives Et 1-cyanocyclopentane-1- α -cyanoglutarate, b.p. $210\text{--}213^\circ/8$ mm., hydrolysed and decarboxylated to cyclopentane-1-carboxylic-1- α -glutaric acid, m.p. $131\text{--}132^\circ$. The Et_2 ester, b.p. $162\text{--}165^\circ/4$ mm., of this, with Na in C_6H_6 , yields Et₂ 1-keto-[0:4:4]-dicyclononane-2:4-dicarboxylate, b.p. $168^\circ/4$ mm., hydrolysed and decarboxylated to 1-keto-[0:4:4]-dicyclononane-4-carboxylic acid, m.p. 67° ; this is reduced (Clemmensen) and the product decarboxylated to [0:4:4]-dicyclononane (cyclopentanespirocyclopentane).

CH. ABS. (r)

Action of N_2O_3 on $\Delta^{1:3}$ -cyclohexadiene. A. S. ONISCHTSCHENKO (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 539—546).— $\Delta^{1:3}$ -cyclohexadiene (I) in AcOH, $\text{C}_5\text{H}_{11}\cdot\text{NO}_2$, and 10% HCl in EtOH at -10° yield the nitrosochloride, m.p. 123° , of (I). (I) in Et_2O and N_2O_3 at -5° yield a ψ -nitrosite (impure), which is reduced (Sn and HCl) to 1:4-diamino- Δ^2 -cyclohexene, +2HCl [platinochloride, aurichloride, both m.p. $<250^\circ$; di-N-benzoyl derivative, m.p. $278\text{--}280^\circ$ (decomp.)], and 1-hydroxy-4-amino- Δ^2 -cyclohexene, +HCl [platinochloride, +2H₂O, decomp. at $222\text{--}223^\circ$; aurichloride, +H₂O, m.p. $187\text{--}190^\circ$ (decomp.)].

R. T.

Sulphonaphthenic acids. S. VON PILAT and M. TURKIEWICZ (Petroleum, 1937, 33, No. 41, 1—4).—

Several chlorinated naphthenic acids and their derivatives were prepared and their properties and behaviour towards alkalis examined. Na sulphonaphthenates were obtained from the Cl_2 -compounds by decomp. with Na_2SO_3 , and the corresponding esters from esters of chloronaphthenic acids. The course of this reaction was examined with regard to the formation of lactones and hydroxy- and olefinocarboxylic acids. The Na salts behave as salts of a strong acid, changing the colours of Me-orange and Congo-red. A study of the saponification products of monochloronaphthenic acids indicates that the Cl is mainly (65%) in the α -position with regard to the CO_2H . The interfacial tension between C_6H_6 and solutions of naphthenates, chloro- and sulphonaphthenates was measured. The first-named cause the greatest mol. lowering of tension.

H. C. R.

Hydrogenation of aromatic hydrocarbons by means of calcium-ammonia. B. A. KAZANSKI and N. V. SMIRNOVA (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 547—554).— H_4 -derivatives are obtained by passing C_6H_6 , PhMe, C_{10}H_8 , or $\Delta^{1:3}$ -cyclohexadiene through a layer of Ca-NH_3 at 0° .

R. T.

Friedel-Crafts synthesis. N. O. CALLOWAY (Chem. Rev., 1935, 17, 327—392).—A general summary.

CH. ABS. (r)

Preparation of bromomesitylene. F. DUKE, H. LEWIS, and R. E. DUNBAR (Proc. S. Dakota Acad. Sci., 1935, 15, 21—23).—Mn is superior to Fe as catalyst in the direct bromination of mesitylene.

CH. ABS. (r)

Halogenation of aromatic and aliphatic compounds. R. ODA and K. TAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 33, 129—208).—Halogenation is usually effected by addition of Br or Cl_2 in AcOH to the org. compounds in AcOH, less frequently in $n\text{-C}_6\text{H}_{14}$ or H_2O ; excess of halogen is determined periodically by addition of KI and titration with $\text{Na}_2\text{S}_2\text{O}_3$. The velocity coeffs., calc. for a bimol. reaction, invariably increase or decrease with time. When bromination occurs instantaneously the reaction is followed by the combined use of KI and Br. These react momentarily and quantitatively, $\text{Br}_2 + \text{KI} = \text{KBr} + \text{IBr}$, but in presence of a very rapidly reacting org. compound some of the Br is utilised thereby and less IBr (which does not react with org. compounds) is produced. The amount of it produced therefore indicates the activity of the org. compound. The following general conclusions are reached. C_6H_6 , halogenobenzene (I), PhNO_2 , BzOH, COPh_2 , and, probably, PhCHO are scarcely brominated. (I) directs towards the *o*- and *p*-, the others towards the *m*-position. PhMe, xylene, C_{10}H_8 , and 1:2:3:4-tetrahydronaphthalene (II) are brominated with moderate rapidity and Me directs to the *o*- and *p*-positions. Anthracene and phenanthrene are brominated very rapidly but the change can be followed iodometrically. Bromination of aromatic NH_2 - and OH-compounds and of true aliphatic, unsaturated compounds such as $\text{CHPh}\cdot\text{CH}_2$ and cyclohexene takes place instantaneously and too rapidly to be followed iodometrically; OH and NH_2 direct to the *o*- and *p*-positions. The theory of alternating polarity is

regarded as incapable of explaining these observations but the electromeric displacement hypothesis accounts for the unusual reactivity of NH_2Ph and PhOH and the disturbing influence of NO_2 , halogen, or CO . The coupling theory of Schmidt is false since it fails to explain the unusual turgidity of PhNO_2 although it appears valid for the directive influence of NO_2 . Schmidt's double linking rule explains satisfactorily the general influence of Me . Thus in PhMe a quantum-mechanical union exists between C of Me and C of the C_6H_5 nucleus united therewith, and hence reactivity is apparent in the *o*- and *p*-positions; this is also the cause of the reactivity of PhMe and (II). Similarly the reactivity of PhOH and NH_2Ph can be explained. If the unshared electron of the N of NH_2Ph is coupled with the *p*-electron of the $\text{C}_{(6)}$ atom, the residual nucleus must assume the form $\text{C} \begin{smallmatrix} \text{C}=\text{C} \\ \text{C}=\text{C} \end{smallmatrix} \text{C}=\text{N}$ or $-\text{C} \begin{smallmatrix} \text{C}=\text{C} \\ \text{C}=\text{C} \end{smallmatrix} \text{C}=\text{N}$ thus explaining the reactivity of NH_2Ph in the *o*- and *p*-positions. This is true also for PhOH . H. W.

Direct conversion of iodic acid and aromatic hydrocarbons into iodonium compounds. I. MASSON and E. RACE (J.C.S., 1937, 1718—1723; cf. A., 1936, 61).— HIO_3 in H_2SO_4 with PhX ($\text{X} = \text{H}, \text{Me}, \text{Cl}, \text{Br}$, or I) yields mainly iodonium radicals ($\text{C}_6\text{H}_4\text{X})\cdot\text{I}^+$, some *p*- $\text{C}_6\text{H}_4\text{XI}$, and unidentified aliphatic degradation products of PhX . The reaction may be used for the detection of aromatic impurity in aliphatic hydrocarbons. With PhOMe and other highly reactive or easily oxidisable derivatives, decomp. takes place, and when X is a *m*-directing substituent (e.g., NO_2) the reaction is almost entirely inhibited. The iodonium salts may be isolated from the reaction by SO_2 , or NaI , or both, to yield diaryliodonium iodides, or by dilution with H_2O to yield the acid sulphates. Since I_2O_3 and H_2SO_4 with PhX afford only pure iodonium compounds in quant. yield, the following mechanism of reaction is suggested: primary deoxidation of HIO_3 to HIO_2 by PhX (which is oxidised to aliphatic substances) followed by $\text{HO}\cdot\text{IO} + 2\text{PhX} \rightarrow (\text{C}_6\text{H}_4\cdot\text{X})_2\cdot\text{I}\cdot\text{OH} + \text{H}_2\text{O}$.

(*p*- $\text{C}_6\text{H}_4\text{Cl}$) $_2\text{I}\cdot\text{HSO}_4$ is converted by H_2O into [(*p*- $\text{C}_6\text{H}_4\text{Cl}$) $_2\text{I}$] $_2\text{SO}_4$, the change being reversed by H_2SO_4 . The normal and acid sulphates are in equilibrium in 6*N*- H_2SO_4 . J. D. R.

Aryl iododihalides as halogenating agents. B. S. GARVEY, jun., L. F. HALLEY, and C. F. H. ALLEN (J. Amer. Chem. Soc., 1937, 59, 1827—1829; cf. Bockemüller, A., 1931, 611).—Various unsaturated compounds [$\text{COPh}\cdot\text{CH}\cdot\text{CHPh}$, (CHPh) $_2$, $\text{CO}(\text{CH}\cdot\text{CHPh})_2$, *trans*-(CHBz) $_2$, Δ^2 -pentene (the only aliphatic hydrocarbon to give a satisfactory product)] add Cl when heated with PhICl_2 in $\text{C}_2\text{H}_4\text{Cl}_2$, the reaction being less vigorous than with Cl_2 ; $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and C_6H_5 are unattacked. PhIF_2 (from PhIO and 46% HF in AcOH) with simple olefines and (CHPh) $_2$ in CHCl_3 gives mixtures; rubber similarly yields an impure F_1 -derivative. Fluorination and/or coupling occurs with some aromatic hydrocarbons. Thus, acenaphthene affords *diacenaphthenyl*, m.p. 174°; pyrene yields *fluoropyrene*,

m.p. 113°, and *dipyrenyl* (?), softens about 250°, molten at 300°; anthrone gives (in one case only) *dianthronyl*, m.p. 360°; anthracene furnishes 9-*fluoroanthracene*, m.p. 110° (oxidised to anthraquinone); benzanthrone affords *Bz-2(or 3)-fluorobenzanthrone*, m.p. 186° (oxidised to anthraquinone-1-carboxylic acid). No reaction occurs between PhIF_2 and various compounds (e.g., C_{10}H_8 , phenanthrene, $\alpha\beta$ -diphenylbutadiene, PhOMe , NHAcPh , anthraquinone). H. B.

Decomposition of iodonium salts. R. B. SANDIN, M. KULKA, and R. MCCREADY (J. Amer. Chem. Soc., 1937, 59, 2014—2015; cf. Lucas *et al.*, A., 1936, 323).— PhIO , *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{IO}_2$, and moist Ag_2O are triturated with a little CHCl_3 ; the aq. extract with KHal affords *phenylanisilyliodonium chloride* (I), *bromide* (II), and *iodide*. Thermal decomp. of (I) and (II) gives mainly *p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{OMe}$ with PhCl and PhBr , respectively, i.e., the more electro-negative anisyl radical remains attached to I. The I in *p*- $\text{C}_6\text{H}_4\text{I}\cdot\text{OMe}$ (not PhI) is eliminated by SnCl_2 in 40% HBr + approx. 75% AcOH ; a quant. procedure is detailed. H. B.

Mechanism of sulphonation of aromatic compounds, and the hydrolysis of their sulphonic acids. V. UFIMTSEV (Prom. Org. Chim., 1937, 4, 157—161).—Theoretical. The stability to hydrolysis of sulphonic acids falls with rise of temp., time of heating, and [H_2SO_4]; as a result, at a given temp., a mixture of isomeric acids is formed, in which the proportion of the acid most resistant to hydrolysis rises with time. The reactions of sulphonation or hydrolysis are not of the first or second order.

R. T.

Salts of nitro-compounds. I. Preparation, alkylation, and acylation of salts of phenylnitroacetonitrile. J. T. THURSTON and R. L. SHRINER (J. Org. Chem., 1937, 2, 183—194).— $\text{CH}_2\text{Ph}\cdot\text{CN}$, KOEt , and *dl*-, *d*-, or *l*-octyl nitrate give the optically inactive *K* salt (I) of $\text{CN}\cdot\text{CHPh}\cdot\text{NO}_2$, considered to have a conjugated *aci*-structure. Neither (I) nor the *Na* salt (II) gives alkyl derivatives with alkyl halides; (II) and Me_2SO_4 yield $\text{CN}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{CN}$. The *Ag* salt (III), however, with MeI forms *aciphenylnitroacetonitrile Me ester*, $\text{CN}\cdot\text{CPh}\cdot\text{N} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OMe} \end{smallmatrix}$, m.p. 41—42°, decomp. on keeping,

of which the *O*-alkyl structure is established by reduction ($\text{PtO}_2\text{-Ac}_2\text{O-H}_2$) to $\text{NHAc}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NHAc}$ (IV), new m.p. 155—155.5° (also synthesised via $\text{NH}_2\cdot\text{CHPh}\cdot\text{CN}$). With CH_2PhCl , (III) gives $\text{CN}\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$, [reduced to (IV)], and PhCHO , by decomp. of an unstable CH_2Ph ester. With BzCl , (II), or better (III), gives a compound, m.p. 116° (decomp.), which is *O*-benzoylphenylnitroacetonitrile, and not the *C*-*Bz* compound, *Ph* ω -nitro- ω -cyano-benzyl ketone (A., 1933, 1163), since reduction ($\text{PtO}_2\text{-Ac}_2\text{O-H}_2$) gives (IV) and BzOH . E. W. W.

Halogenation of acenaphthene. M. DASCHESKI and A. KARISCHIN (Prom. Org. Chim., 1937, 4, 109—113).—Acenaphthene in EtOH (at the b.p.) and Cl_2 (2 mols.) give chiefly 4 : 5-dichloroacenaphthene (I) in 55% yield, together with 4-chloro- and traces of trichloro-acenaphthene. (I) in AcOH and $\text{K}_2\text{Cr}_2\text{O}_7$

yield 4:5-dichloroacenaphthenequinone and 4:5-dichloronaphthalic acid.

R. T.

[Pyrene syntheses.] W. QUIST (Annalen, 1937, 532, 302).—Syntheses of pyrene (cf. Vollmann *et al.*, A., 1937, II, 450) from 2:6:2':6'-tetramethyl- and 2:6'-diethyl-diphenyl and from phenanthrene and C_2H_4 have been described by Mattsson (Diss., Helsingfors, 1905).

H. W.

Derivatives of 1:2-benzpyrene. A. WINDAUS and S. RENNHAKE (Z. physiol. Chem., 1937, 249, 256—266).—1:2-Benzpyrene in CS_2 with Br at 5° gives the Br_3 -derivative (I), m.p. 298—298.5°; in AcOH with conc. HNO_3 at room temp. a NO_2 -derivative (II), m.p. 250.5—251°; with conc. HNO_3 at approx. 100° a $(NO_2)_2$ -derivative (III), m.p. 286.5° (decomp.); with conc. H_2SO_4 and Ac_2O a monosulphonic acid (IV), m.p. 146—148° (*Me* ester, m.p. 206°; *K* and *Na* salts); and with Ac_2O and $AlCl_3$ acetylbenzpyrene, m.p. 186—186.5°, which, in dioxan, with aq. NaOH and conc. I in aq. KI at $>60^\circ$ followed by treatment with CH_2N_2 yields the *Me* ester, m.p. 151—151.5°, of the corresponding carboxylic acid. (II) boiled with $NHPh \cdot NH_2$ for 5 hr. gives the corresponding NH_2 -compound (V), m.p. 231° (decomp.) [*Ac* derivative, m.p. 217.5°; *picrate*, m.p. 180° (decomp.)]. The compounds (I)—(V) are not carcinogenic.

W. McC.

Pharmaceutically important arsenic compounds. II. K. BRAND and E. ROSENKRANZ (Pharm. Zentr., 1937, 78, 685—691; cf. B., 1932, 1104).—The preps. of the following are described: NH_4 meta-arsenite, NH_4AsO_2 , cyclohexylammonium meta-arsenite and its $HAsO_2$ additive compound, $C_6H_{11} \cdot NH_3 \cdot AsO_2$, $HAsO_2$, and $NH_4Cl \cdot As_2O_3$.

E. H. S.

Rearrangement of N-chloroacetanilide. R. S. HALFORD and J. C. HORNEL (J. Amer. Chem. Soc., 1937, 59, 1613—1615).—The rearrangement to *o*- and *p*-chloroacetanilide in aq. EtOH containing H_2SO_4 has been reinvestigated kinetically, using radioactive Cl' as catalyst (cf. A., 1937, II, 87). Equal amounts of *o*- and *p*-compound are produced. The change in radioactivity of Cl' in solution during the progress of the reaction rules out the possibility of an intramolecular mechanism. A Cl' -intermediate mechanism is proposed.

E. S. H.

Action of primary amines on dibromodiethylenediamine cobaltibromide. A. ABLOV (Bull. Soc. chim., 1937, [v], 4, 1783—1793).—Interaction of dibromodiethylenediamine cobaltibromide, $[Co en_2 Br_2]Br$, and the appropriate amine in aq. EtOH yields pentamminocobaltic compounds of the structure $[Co en_2(R)Br]Br_2$ (other salts prepared are indicated in parentheses) where R is NH_2Ph , $m-C_6H_4Me \cdot NH_2$ (dinitrate, di-iodide), $p-C_6H_4Me \cdot NH_2$ (di-iodide), $o-NH_2 \cdot C_6H_4 \cdot OMe$ (di-iodide, dinitrate), $o-NH_2 \cdot C_6H_4 \cdot OEt$ (di-iodide, dinitrate), $m-C_6H_4Cl \cdot NH_2$ (di-iodide), $p-C_6H_4Cl \cdot NH_2$, $m-C_6H_4Br \cdot NH_2$ (di-iodide), $p-C_6H_4Br \cdot NH_2$, $p-C_6H_4I \cdot NH_2$, $\beta-C_{10}H_7 \cdot NH_2$, NH_2Et (di-iodide, dinitrate). With $\alpha-C_{10}H_7 \cdot NH_2$ and $o-C_6H_4Me \cdot NH_2$, $[Co en_2]Br_3$ is formed; $o-C_6H_4Cl \cdot NH_2$ does not give a derivative, and with *o*-phenanthroline $[Co en_2(C_{12}H_8N_2)]Br_3$ results.

T. D. R.

Anilides and phenylhydrazides of alanine, glycine, and leucine derivatives.—See A., III, 393.

Relative hypnotic effects of some carbamides of varied types. A. M. HJORT, E. J. DE BEER, J. S. BUCK, W. S. IDE, and D. W. FASSETT (J. Pharm. Exp. Ther., 1937, 61, 175—181).—The following carbamides have been prepared: $\beta\beta\beta$ -tribromoethyl-, m.p. 174°; $\beta\beta$ -dibromopropyl-, m.p. 110°; $\beta\beta\gamma$ -tribromopropyl-, m.p. 139°; *as-m*-chlorophenylmethyl-, m.p. 98—99°; *as-p*-bromophenylmethyl-, m.p. 110°; *p*-dimethylaminophenyl-, m.p. 181°; *as-p*-dimethylaminophenyl-*n*-propyl-, m.p. 125°; *as-p*-hydroxyphenyl-*n*-propyl-, m.p. 191°; *as-m*-carboxyphenylethyl-, m.p. 210°; *as-o*-, m.p. 110°, and *p*-ethylphenylisopropyl-, m.p. 104°; *as- α* -naphthylmethyl-, m.p. 119°; *as- α* -naphthylethyl-, m.p. 141°; *as- β* -naphthylmethyl-, m.p. 110°; *as- β* -naphthylethyl-, m.p. 99°; *o*- and *p*-phenylenedi-; bis-pentamethylene- (I), m.p. 104°; Δ^2 -cyclohexenyl-, m.p. 197°; *N-p*-anisyl-*N*-s-diethylisothio- (hydrochloride) (II), m.p. 150°. The hypnotic action of carbamide derivatives is increased by the introduction of halogen atoms. (I), from piperidine, is less potent than the Δ^2 -cyclohexenyl- and phenyl-carbamides. The introduction of OH or CO_2H into the ring of arylcarbamides much decreases their activity. (II) is a convulsant and relatively toxic.

W. O. K.

Constitution and reactions of thiocarbonyl tetrachloride. IV. Reaction with secondary and tertiary amines. C. S. ARGYLE and G. M. DYSON (J.C.S., 1937, 1629—1634; cf. A., 1937, II, 375, 411).—*sec*-.Dialkyl- and arylalkyl-amines and $CCl_3 \cdot SCl$ (I) give unstable compounds, $CCl_3 \cdot S \cdot NRR'$; diarylamines give $CHPh_2$ dyes and substances containing at least one $NRR' \cdot C$; *tert*. amines give dyes of the crystal-violet type by way of substances, $NR_2 \cdot C_6H_4 \cdot S \cdot CCl_3$, the CCl_3 of which provides the *tert*. C of the $CHPh_2$ series. The appropriate *sec*. amine and (I) in Et_2O -aq. NaOH at 30° give *S*-dimethyl-, b.p. $74^\circ/15$ mm., -diethyl-, b.p. $96^\circ/15$ mm., -diisobutyl-, b.p. $127^\circ/15$ mm. (decomp.), -methyl-anilino-, and -methyl-*p*-toluidino-aminotrichloromethylthiol; the arylalkyl compounds decompose when distilled and others of this type, although prepared, were very unstable. These thiols with HCl in ligroin regenerate the amine and (I), are reduced by $Zn \cdot AcOH$ to $MeSH$, are hydrolysed slowly by hot H_2O and rapidly by 20% aq. alkali to RCN and $RCNS$, and with an excess of an arylamine in ligroin give triarylguanidines in varying yield. $NHPh_2$ with $CSCl_2$ or (I) gives $NN'N''$ -triphenylpararosaniline hydrochloride (II) and a red compound (III), (?) $NPh_2 \cdot C(C_6H_4 \cdot NHPh) \cdot C_6H_4 \cdot NHPhCl$. The structure of (III) is based on its conversion by H_2SO_4 at 70° into a sulphate and monosulphonic acid, by fuming $HNO_3 \cdot AcOH$ at 100° into $NO \cdot N(C_6H_4 \cdot NO_2 \cdot p)_2$ [with NH_2Ph at 120° gives $NH(C_6H_4 \cdot NO_2)_2$], by $KMnO_4$ into $PhNC$ (in alkali) or $NHPh_2$ (in acid), and by dry distillation into $NHPh_2$; $AcCl \cdot Ac_2O$ reacts with (III), but no *Ac* derivative could be isolated. Both (II) and (III) are also obtained from $NHPh_2$ with $CCl_3 \cdot NO_2$, $CCl_3 \cdot SO_2Cl$, or $p-C_6H_4Me \cdot S \cdot CCl_3$ at 150° . Reaction probably proceeds by way of $CS(NPh_2)_2$ which suffers *p*-rearrangement of the semidine-

benzidine type to $\text{NPh}_2\cdot\text{CS}\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$ and thence to (II). NPhMe_2 and (I) at $<20^\circ$ give S-p-dimethylaminophenyltrichloromethylthiol (IV), $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CCl}_3$, m.p. 71° [$(\text{NO}_2)_2$, m.p. 123° , and Br-derivative, m.p. 146° (decomp.)]; hydrochloride, m.p. 129 – 130° (decomp.), with $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ and crystal-violet. The p-di-ethyl-, m.p. 44° , -n-propyl-, -n-butyl-, and p-methylethyl-thiols, oils, were similarly prepared. (IV) is hydrolysed by H_2O to p-NMe $_2\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ (V) (Pb salt), which is oxidised by air to bis-p-dimethylaminophenyl sulphide, m.p. 118° , also obtained from S_2Cl_2 and NPhMe_2 . With NH_2Ph in EtOH (IV) and its analogues give S-p-di-methyl- (VI), m.p. 175° , -ethyl-, m.p. 128° , and -n-propylaminophenyl-NN'-diphenylisothiocarbamide, $\text{NR}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}(\text{NPh})\cdot\text{NHPh}$, m.p. 125° ; with other arylamines (IV) gives S-p-dimethylaminophenyl-NN'-di-p-tolyl-, m.p. 142° , -p-chlorophenyl-, m.p. 157° , and -p-bromophenyl-isothiocarbamide, m.p. 167° . With $\text{NH}_2\cdot\text{EtOH}$ at 120° (VI) gives (V) and $\text{NH}_2\cdot\text{C}(\text{NHPh})_2$, and with NH_2Ph at 170° (V) and $\text{NPh}_2\cdot\text{C}(\text{NHPh})_2$; with $\text{CHCl}_3\cdot\text{KOH}$ it gives PhNC , and with $\text{Sn}\cdot\text{HCl}$ NH_2Ph , but it is unaffected by $<80\%$ KOH ; it is also obtained from $\text{NPh}_2\cdot\text{CCl}\cdot\text{NHPh}$ and $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{SK}$ in hot EtOH. NPhMe_2 , (IV), and AlCl_3 at 100° give p-C $_6\text{H}_4\text{Me}\cdot\text{SH}$ and crystal-violet, and NHPH_2 reacts similarly. NPh_2Me and (I) at 100 – 130° give NN'N''-triphenyl-NN'N''-trimethyl-pararosaniline hydrochloride; NPh_3 at 180° gives hexaphenylpararosaniline hydrochloride, converted into the carbinol; arylalkylamines react with partial dealkylation and $\text{N}(\text{CH}_2\text{Ph})_3$ similarly gives CH_2PhCl and CSCl_2 . R. S. C.

Phenylthiocarbamides. The triad -N·C·S-.
IV. Action of silver nitrate on phenylthiocarbamide. V. Action of nitrous acid on N-phenyl-N-methylthiocarbamide. K. B. LAL and H. KRALL (J. Indian Chem. Soc., 1937, 14, 474–477, 478–485).—IV. AgNO_3 and $\text{NHPH}\cdot\text{CS}\cdot\text{NH}_2$ (I) in acid solution give several complexes. With excess of aq. AgNO_3 , the compound $\text{NHPH}\cdot\text{CS}\cdot\text{NH}_2\cdot\text{AgNO}_3$, decomp. 132 – 134° (which takes up further AgNO_3), is formed, which with KSCN (II) yields a compound $\text{NHPH}\cdot\text{CS}\cdot\text{NH}_2\cdot\text{AgSCN}$. Thus by Volhard's method (II) can be determined in presence of (I), provided (I) is $<$ equiv. to (II), with which it is equimolecularly pptd.

V. $\text{NPhMe}\cdot\text{CS}\cdot\text{NH}_2$ (III) and HNO_2 in strongly acid solution give phenylmethylformamidine disulphide, $[\text{NPhMe}\cdot\text{C}(\text{NH})\text{S}]_2$ (perchlorate, m.p. 143° ; picrate, m.p. 140°), and NO ; in presence of AcOH , compounds, m.p. 199° (decomp.), and 205 – 210° , and N_2 , are formed, apparently by way of $\text{NPhMe}\cdot\text{CS}\cdot\text{OH}$. Acids presumably facilitate the change $\text{NPhMe}\cdot\text{CS}\cdot\text{NH}_2 \rightarrow \text{NPhMe}\cdot\text{C}(\text{NH})\cdot\text{SH}$. No diazo-thiol is formed in the reaction between (III) and HNO_2 . E. W. W.

Some nuclear alkyl derivatives of β -phenylethylamine. J. H. SPEER and A. J. HILL (J. Org. Chem., 1937, 2, 139–147).—The following are prepared (h. = hydrochloride; p. = picrate): β -o-tolylethylmethylamine, b.p. $99^\circ/12$ mm. (h., m.p. 167° ; p., m.p. 114 – 115°), β -m-, new b.p. 98 – $99^\circ/12$ mm. (cf. A., 1926, 512) (h., new m.p. 143°), and β -p-

tolylethylmethylamine (loc. cit.); β -o-, b.p. $120.5^\circ/14$ mm. (h., m.p. 147.5° ; p., m.p. 110°), β -m-, b.p. $120^\circ/15$ mm. (h., m.p. 148° ; p., m.p. 95°), and β -p-tolylethylamine, b.p. $119^\circ/14$ mm. (h., m.p. 115 – 116° ; p., m.p. 132°); β -m-, b.p. $100^\circ/9$ mm. (h., m.p. 161 – 162° ; p., m.p. 133°), and β -p-tolylethylamine, b.p. $107^\circ/12$ mm. (h., m.p. 203 – 204° ; p., m.p. 126°); benzyl-, b.p. 165 – $167^\circ/4$ mm. (h., m.p. 232 – 234° ; p., m.p. 125°), and diphenylmethyl- β -p-tolylethylamine, m.p. 73.5° , b.p. 193 – $195^\circ/2.5$ mm. (h., m.p. 256° ; p., m.p. 155°); β -diethylamino- β' -tolylethylamine, b.p. 131 – $134^\circ/3$ mm. (dihydrochloride, m.p. 124 – 125°); β -p-tolylethyl-di-n-butylamine, m.p. 120 – $122^\circ/2.5$ mm. (h., m.p. 93° ; p., m.p. 62 – 63°); 1- β -p-tolylethylpiperidine, b.p. $118^\circ/4$ mm. (h., m.p. 212° ; p., m.p. 144°); β -p-ethylphenyl-, b.p. $97^\circ/8$ mm. (h., m.p. 208° ; p., m.p. 168°), and methyl- β -p-ethylphenyl-ethylamine, b.p. 90 – $91^\circ/4.5$ mm. (h., m.p. 192 – 193° ; p., an oil); β -o-, b.p. $155^\circ/4$ mm. (h., m.p. 169 – 170° ; p., m.p. 178 – 179°), and β -p-benzylphenylethylamine, b.p. 178 – $181^\circ/8$ mm. (h., m.p. 222 – 224° ; p., m.p. 154 – 155°); β -o-, b.p. 146 – $148^\circ/3$ mm. (h., m.p. 180° ; p., m.p. 169 – 171°), and β -p-benzylphenylethylmethylamine, b.p. 145 – $146^\circ/3$ mm. (h., m.p. 192° ; p., m.p. 93 – 94°); β -o-, b.p. $157^\circ/3$ mm. (h., m.p. 122° ; p., m.p. 143 – 144°), and β -p-benzylphenyltriethylamine, b.p. 169 – $170^\circ/3$ mm. (h., m.p. 136.5° ; p., oil); and β -p-(β' -phenylethyl)-, m.p. 49° , b.p. $160^\circ/2$ mm. (h., m.p. 213 – 215° ; p., m.p. 135°), and methyl- β -p-(β' -phenylethyl)-phenylethylamine, b.p. 152 – $155^\circ/2.5$ mm. (h., m.p. 197° ; p., m.p. 115 – 116°).

The amines are obtained from the substituted phenylethyl bromides, prepared (PBr_3) from the alcohols which result from action of $(\text{CH}_2)_2\text{O}$ on the Mg derivatives of substituted bromobenzenes. The following intermediates are also described: p-C $_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ (I) (A., 1932, 158), b.p. $165^\circ/3$ mm. (oxime, m.p. 137°); p-bromodiphenylmethane, b.p. $162^\circ/13$ mm. (from $\text{COPh}\cdot\text{C}_6\text{H}_4\text{Br}$, HI, and P); p-bromo-s-diphenylethane, m.p. 32° , b.p. $143^\circ/3$ mm. [obtained with $(\text{CH}_2\text{Ph})_2$ from (I)]; β -p-ethyl-, b.p. 98 – $101^\circ/4$ mm. (phenylurethane, m.p. 104.5°), β -o-, b.p. $162^\circ/3$ mm. (phenylurethane, m.p. 124°), and β -p-benzyl- (II), b.p. $172^\circ/4.5$ mm. (phenylurethane, m.p. 93°), and β -p- β' -phenylethyl-phenylethyl alcohol (III), m.p. 67 – 68° , b.p. $172^\circ/3$ mm. (phenylurethane, m.p. 107°). As by-products with (II) and (III), pp'-dibenzyl-, m.p. 113° , b.p. 190 – $215^\circ/5$ mm., and pp'-di- β -phenylethyl-diphenyl, m.p. 146° , are obtained. 1-Ethyl-4- β -bromoethylbenzene has b.p. 84 – $86^\circ/3$ mm. As a by-product of the action of PBr_3 on (III), the acid phosphite, no m.p. $<300^\circ$, of (III) is obtained. $\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$ and p-C $_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ give β -p-tolylethylphthalimide, m.p. 117° , hydrolysed to the β -p-tolylethylmonoamide, m.p. 150° , of phthalic acid, and to the amine. E. W. W.

2-Methyl- α -naphthylamine-4-sulphonic acid. H. E. FIERZ-DAVID and E. MANNHART (Helv. Chim. Acta, 1937, 20, 1024–1040).—1-Nitro-2-methylnaphthalene, b.p. 185 – $186^\circ/18$ mm., m.p. 80 – 81° , is obtained in 60% yield by gradual addition of fuming HNO_3 to 2-C $_{10}\text{H}_7\text{Me}$ in AcOH at 0° to 5° and subsequent gradual heating to 80° or from 2-

$C_{10}H_7Me$ and conc. HNO_3 at $70-75^\circ$. It is reduced by Fe in neutral solution or by $SnCl_2-HCl$ in $AcOH$ to 2-methyl- α -naphthylamine, b.p. $165^\circ/12$ mm. (Ac derivative, m.p. 188°). A hydrazo-derivative is not obtained in alkaline solution. Gradual addition of the base to 50% H_2SO_4 at $110-140^\circ$ gives the *H* sulphate, which passes at $180^\circ/vac.$ into 2-methyl- α -naphthylamine-4-sulphonic acid. This can be diazotised in the usual manner and converted into azo-dyes with $\alpha-C_{10}H_7\cdot OH$, *R* acid, chromotropic acid, 1:5- $OH\cdot C_{10}H_6\cdot SO_3H$, Schäffer and Neville-Winther acid, SS-acid, acetyl-H-acid, phenylmethylpyrazolone, and *p*-sulphophenylmethylpyrazolone. The dyes are somewhat yellower than those derived from 1:4- $NH_2\cdot C_6H_4\cdot SO_3H$, are more even, and usually somewhat faster to light. Unlike the latter, they are unaffected by CrO_3 , since the presence of Me prevents the formation of OH *ortho* to N_2 which is essential to after-chroming. This view is confirmed by treatment of the dye from 1:4- $NH_2\cdot C_{10}H_6\cdot SO_3H$ and 1:5- $OH\cdot C_{10}H_6\cdot SO_3H$ in substance with CrO_3 and reduction of the product to 1:2:4- $NH_2\cdot C_6H_5(OH)\cdot SO_3H$; the hypothesis of Rosenhauer (A., 1930, 81) is thus established.

Aromatic nitro-derivatives. XIII. Substituted α -naphthylamines. A. MANGINI (Atti R. Accad. Lincei, 1937, [vi], 25, 387-391).—Reaction products from 1:2:4- $C_{10}H_5Cl(NO_2)_2$ and amines are described, as follows: N-2:4-dinitro-1-naphthyl-ethyl-, m.p. $165.5-166.5^\circ$, and -allyl-amine, m.p. $146-147^\circ$, and -piperidine, m.p. $135-136^\circ$; N-m-hydroxyphenyl-2':4'-dinitronaphthylamine, m.p. $176-177^\circ$; o-, m.p. 260° (decomp.) (*Et* ester, m.p. $185-186^\circ$), and m-2':4'-dinitro-1'-naphthylaminobenzoic acid, m.p. 250° (decomp.) (*Et* ester, m.p. $152.5-153.5^\circ$); N-2':4'-dinitro-1'-naphthylsulphanilic acid, m.p. 190° (decomp.); p-2':4'-dinitro-1'-naphthyl-amino-acetophenone, new m.p. $170-171^\circ$ (cf. A., 1936, 75) [*p*-nitrophenylhydrazone, m.p. 255° (decomp.)], and -benzophenone, m.p. $200-201^\circ$ (decomp.), and 2-2':4'-dinitro-1'-naphthylaminopyridine, m.p. $189-190^\circ$ (decomp.).

[C-Alkyl] aniline derivatives.—See B., 1937, 1023.

Mononitroalkylanilines, nitroalkylacylanilines, and derivatives thereof.—See B., 1937, 1023.

Arylnaphthylamines.—See B., 1937, 1023.

Amidines. II. Diamidines from di-imido-chlorides derived from diamines. H. K. S. RAO and T. S. WHEELER (J.C.S., 1937, 1643-1645).—(*p*- $NHBz\cdot C_6H_4$) $_2$ and PCl_5 in $PhNO_2$ give dibenzbenzididedi-imidochloride, (*p*- $C_6H_4ClN\cdot C_6H_4$) $_2$, m.p. 212° , which with NH_3 -MeOH gives NN'-di-(α -aminobenzylidene)benzidine, m.p. 252° , with KCN -MeOH gives NN'-di-(α -cyanobenzylidene)benzidine, m.p. 252° , with the appropriate base in $NPhEt_2$ at 100° gives NN'-di-(α -o-chloroanilino-, m.p. 234° [picrate, m.p. $229-230^\circ$ (decomp.)], -methylanilino-, m.p. 234° [picrate, m.p. 248° (decomp.)], -ethyl-anilino-, m.p. 203° [picrate, m.p. 235° (decomp.)], -benzylanilino-, m.p. 174° [picrate, m.p. 185° (decomp.)], -diphenylamino-, m.p. 262° (picrate, m.p. 234°), -ethyl-o-toluidino-, m.p. 200° (picrate, an oil), and -ethyl-p-toluidino-
T (A., II.)

benzylidene)benzidine, m.p. 221° (picrate, an oil). $p-C_6H_4(NH_2)_2$ gives similarly dibenz-p-phenylenediamidedi-imidochloride, m.p. 176° , NN'-di-(α -methyl-anilino-, m.p. 264° [picrate, m.p. 243° (decomp.)], -benzylanilino-, m.p. 203° [picrate, m.p. 220° (decomp.)], -methyl-o-toluidino-, m.p. 227° [picrate, m.p. 236° (decomp.)], -ethyl-o-toluidino-, m.p. 186° [picrate, m.p. 237° (decomp.)], and NN'-di-(α -cyano-benzylidene)-p-phenylenediamine, m.p. 236° . $m-C_6H_4(NH_2)_2$ and PCl_5 alone, when heated, give dibenz-m-phenylenediamidedi-imidochloride, m.p. 86° , and thence di-(α -benzylanilinobenzylidene)-m-phenylenediamine, m.p. $129-130^\circ$ (picrate, a paste). R. S. C.

Pyrolytic products of azobenzene. L. F. BOUL-LION and A. M. PARDEE (Proc. S. Dakota Acad. Sci., 1935, 15, 27-28).—The decomp. temp. is 460° ; C_6H_6 , NH_3Ph , Ph_2 , $NHPh_2$, anthracene, phenanthrene, H_2CN , NH_3 , and N_2 are formed.

CH. ABS. (r)

Chloroamines. I. Azobenzene-p-sulphonic acid and certain of its derivatives. A. CHRZASZCZEWSKA and C. DOBROWOLSKI (Rocz. Chem., 1937, 17, 411-422).—(NPh) $_2$ and oleum at $>80^\circ$ yield azobenzene-p-sulphonic acid, $+3H_2O$ (I) (*K*, $+2H_2O$, and *Na* salts), differing from that described by Janovski (A., 1882, 834) in that it decomposes at 130° , in giving a cryst. chloride, m.p. $124.4-125^\circ$ (lit., m.p. 82°), and in giving an amide (II), m.p. $224.8-225.5^\circ$ (cf. Skandarov, J. Russ. Phys. Chem. Soc., 1870, 643). (II) and aq. $NaOCl$ yield the *Na* salt of azobenzene-p-sulphonchloroamide, $+3H_2O$, whilst when $AcOH$ is added to (II) in presence of excess of $NaOCl$ the product is azobenzene-p-sulphon-dichloroamide, m.p. $111.6-112.4^\circ$. (I) is possibly a stereoisomeride of Janovski's acid. R. T.

Crystalline liquid combinations of p-azocinnamic esters with p-azophenol derivatives. Processes of association. D. VORLÄNDER [with R. WILKE, U. HABERLAND, and K. OST] (Ber., 1937, 70, [B], 2096-2108).—Combinations with cinnamic esters are peculiarly adapted to the development of $>$ two cryst. liquid phases or forms. Comparison with benzoic esters shows that this may be due to $\cdot C\cdot C\cdot$ in conjunction with the other associates, the C_6H_6 nucleus, $\cdot N\cdot N\cdot$, $\cdot CH\cdot N\cdot$, $\cdot CO\cdot$, etc. Derivatives of β -phenylpropionic esters are less suitable. The cryst. liquid properties are related to the complete mol. and all its parts. Polymorphous cryst. liquid phenomena can depend stepwise on definite individual parts of the mol. which with falling temp. become successively operative until the whole mol. comes into action and co-operation subsequently exists. As the temp. rises the formation of the cryst. liquid occurs with the distribution over the complete mol. of the many at. linkings in the solid crystal. With the liberation of definite individual portions of the field of union, a second cryst. liquid form can result and so forth until previously to the passage into the amorphous state the remnants of the regions of union become disrupted. According to röntgenographic observations mol. association and union does not cease with the incidence of the amorphous state. The thermostable arrangement of the active portions of the mol. in the cryst. solid as in the cryst. liquid

phase passes in the amorphous material into a condition of max. disorder, since the points of union between the mols. can vary at every temp. and time so that there are no defined transition points or places of union, and no polymorphism. The following appear new: *p-p-hydroxybenzeneazocinnamic acid*, decomp. $>240^\circ$ (corr.), not cryst. liquid (*Et* ester, m.p. $156-158^\circ$); *p-p-methoxybenzeneazocinnamic acid*, decomp. $>255^\circ$ (corr.) after softening at 250° [*Me* ester, m.p. $218-220^\circ$ (corr.); *Et* ester, m.p. 142° (corr.) after softening at 115°]; *p-p-ethoxybenzeneazocinnamic acid* (*Et* ester having three cryst. liquid phases); *Et p-cinnamateazo-p'-phenyl acetate*, m.p. $137-139^\circ$, flowing at $150-152^\circ$ and transparent liquid at 161° (corr.); *Et p-cinnamateazo-p'-phenyl ethyl carbonate*, m.p. 158° after softening at 116° ; *pp'-diethylcarbonatoazobenzene*, m.p. 123° and 98° ; *Et p-cinnamateazo-p'-phenyl benzoate*, m.p. 220° (corr.) after softening at 140° , having three enantiotropic cryst. liquid phases and two cryst. solid forms; *pp'-dibenzoyloxyazobenzene*, m.p. 268° and 216° ; *Et p-cinnamateazo-p'-phenyl benzenesulphonate*, m.p. 110° , and *dimethylaniline*, m.p. $164-166^\circ$; *p-azobenzylidenedimalonic acid*; *p-azocinnamic acid*, m.p. about 290° [corresponding *chloride*, *Et*₂ ester, softens at 157° and becomes transparent at 280° (corr.), *Pr*₂ ester, m.p. 120° and 209° (corr.), and *Me*₂ ester, m.p. 237° and 249° (corr.)]. H. W.

Two new colour indicators from β -naphthylamine. H. EICHLER (Chem.-Ztg., 1937, 61, 797-798).—Azo-dyes formed by coupling diazotised anthranilic and sulphanilic acids, respectively, with β -C₁₀H₇NH₂ may be used as acidimetric indicators.

J. S. A.

Action of hydrazine and methylhydrazine on 3-chloro-4:6-dinitrophenetole and 1-chloro-2:4-dinitronaphthalene and derivatives of the resulting compounds. J. L. ROBERT (Rec. trav. chim., 1937, 56, 909-918; cf. A., 1937, II, 238).—1:3:4:6-C₆H₂Cl₂(NO₂)₂ and NaOEt-EtOH at 5° and finally at 100° give 3-chloro-4:6-dinitrophenetole (I), m.p. 112° , converted by N₂H₄.AcOH in EtOH at 100° into 4:6-dinitro-3-ethoxyphenylhydrazine, m.p. 202° , which on prolonged treatment with the reagent gives small amounts of 4:6-dinitro-1:3-dihydrazinobenzene, explodes at 196° . 3-Chloro-4:6-dinitrophenylhydrazine and NaOEt give 5-chloro-6-nitrobenziminazole, violent decomp. 158° (*Na* salt, m.p. 323°). *N'*-Acetyl-4:6-dinitro-3-ethoxyphenylhydrazine is described. (I) with NHMe.NH₂ in boiling EtOH affords α -4:6-dinitro-3-ethoxyphenyl- α -methylhydrazine, m.p. 151° (block) (*Ac* derivative, m.p. 206°). 1-Chloro-2:4-dinitronaphthalene and N₂H₄.H₂O in EtOH give various reduction and condensation products but replacement of Cl by NH.NH₂ does not occur; under similar conditions NHMe.NH₂.AcOH affords α -2:4-dinitronaphthyl- α -methylhydrazine, m.p. 152° (block). 4:6-Dinitro-3-ethoxyphenylhydrazones, 4:6-dinitro-3-ethoxyphenyl- α -methylhydrazones, and 2:4-dinitronaphthyl- α -methylhydrazones of the following substances have been prepared (m.p. are recorded in this sequence): CH₃O, m.p. $143-144^\circ$, $142-143^\circ$, 100° and 130° ; MeCHO, m.p. 154° , $113-116^\circ$, 127° ;

COMe₂, m.p. $143-145^\circ$, $121-124^\circ$, 183° ; COEt₂, m.p. $107-110^\circ$, $62-64^\circ$, 88° ; Me hexyl ketone, m.p. 78° , $62-64^\circ$, and 54° ; CH₃Ac.CO₂Et, m.p. $153-156^\circ$, 104° . —; heptaldehyde, m.p. $108-109^\circ$, $86-87^\circ$, 85° ; COPhMe, m.p. $220-223^\circ$, 141° , 182° ; PhCHO, m.p. 248° , $171-172^\circ$, 203° ; *o*-C₆H₄Cl-CHO, m.p. $242-245^\circ$, 213° , 176° ; *m*-C₆H₄Cl-CHO, m.p. $244-249^\circ$, $174-176^\circ$, 157° ; *p*-C₆H₄Cl-CHO, m.p. 277° , $218-220^\circ$, 230° ; *o*-NO₂-C₆H₄-CHO, m.p. 200° , $235-237^\circ$, 178° ; *m*-NO₂-C₆H₄-CHO, m.p. 287° , $236-237^\circ$, 212° ; *p*-NO₂-C₆H₄-CHO, m.p. 336° , $250-255^\circ$, 269° ; *o*-OH-C₆H₄-CHO, m.p. 284° , 162° , 206° ; *p*-OH-C₆H₄-CHO, m.p. 263° , 239° , 209° ; *p*-OMe-C₆H₄-CHO, m.p. 242° , $204-205^\circ$, 188° ; *p*-C₆H₄Me-CHO, m.p. $255-259^\circ$, 186° , 183° ; *p*-C₆H₄Pr ^{β} -CHO, m.p. $240-242^\circ$, 164° , 141° ; 4-hydroxy-3-methoxybenzaldehyde, m.p. $252-255^\circ$, 156° , 175° ; 3:4-CH₂O₂-C₆H₃-CHO, m.p. 279° , $191-192^\circ$, 185° ; furfuraldehyde, m.p. $225-228^\circ$, 139° , 202° ; 5-methylfurfuraldehyde, m.p. 199° and $237-239^\circ$, 173° , 167° and 175° ; 5-hydroxymethylfurfuraldehyde, m.p. $177-180^\circ$, $136-137^\circ$, 122° . The colours and solubilities of the compounds are tabulated. H. W.

Mechanism of the diazoaminobenzene conversion. H. V. KIDD (J. Org. Chem., 1937, 2, 198-208; cf. A., 1933, 1044; 1936, 465).—Diazoaminobenzene (I) with conc. HCl at $<0^\circ$, followed by β -C₁₀H₇.OH-NaOH, gives 1-benzeneazo- β -naphthol (II) (91% yield) and NH₂Ph (96% yield as hydrochloride). A solution of NH₂Ph (1 mol.) in aq. HCl (2 mols.) at -2° treated with NaNO₂ (0.5 mol.) and kept in the dark at 0° for 7 days slowly deposits aminoazobenzene (III). The amount of PhN₂Cl, determined as (II), decreases by 75% on keeping for 12 days at 0° ; only 14% is converted into (III). Theories of the conversion of diazoamino-compounds are reviewed; that of unstable intermediates is less satisfactory than that of primary fission and subsequent *p*-combination. The reaction mechanism is discussed from the electronic viewpoint, with special reference to *p*-C₆H₄Me.NH.N:NHPh. E. W. W.

Condensation of tertiary heptyl alcohols with phenol in presence of aluminium chloride. R. C. HUSTON and G. W. HEDRICK (J. Amer. Chem. Soc., 1937, 59, 2001-2003; cf. A., 1936, 602).—The following are prepared from PhOH (0.3 mol.), the *tert.* alcohol quoted (0.25 mol.), and AlCl₃ (0.125 mol.) in light petroleum at $0-30^\circ$: γ -*p*-hydroxyphenyl- γ -methylhexane (from CMeEtPr ^{α} .OH), b.p. $124.6^\circ/4$ mm., $278.5^\circ/748.5$ mm. (*benzoate*, m.p. $38-39^\circ$; *o*-chlorobenzoate, m.p. $25-26^\circ$; α -naphthylcarbamate, m.p. 82.3°); β -*p*-hydroxyphenyl- β -methylhexane (from CMe₂Bu ^{α} .OH), b.p. $123.5^\circ/4$ mm., $277^\circ/749.5$ mm., m.p. $16-17^\circ$ (*benzoate*, m.p. $36-37^\circ$; *o*-chlorobenzoate, b.p. $177-179^\circ/2$ mm.; α -naphthylcarbamate, m.p. $110-111^\circ$); β -*p*-hydroxyphenyl- β -dimethylpentane (from CMe₂Bu ^{β} .OH), b.p. $115-117^\circ/4$ mm., $273^\circ/748.5$ mm., m.p. $31-32^\circ$ (*benzoate*, m.p. $71-72^\circ$; *o*-chlorobenzoate, m.p. $51-52^\circ$; α -naphthylcarbamate, m.p. $114-115^\circ$); γ -*p*-hydroxyphenyl- γ -dimethylpentane [from CMeEtPr ^{β} .OH (prep. from COMePr ^{α} and MgEtBr)], b.p. $125-127^\circ/4$ mm., $272^\circ/748.5$ mm., m.p. $42-43^\circ$ (*benzoate*, m.p. $40-41^\circ$; *o*-chlorobenzoate, m.p. $42-43^\circ$; α -naphthylcarbamate,

m.p. 112—113°; β -*p*-hydroxyphenyl- β - γ -dimethylpentane (from *sec*-BuCMe₂·OH), b.p. 117—119°/4 mm., 281°/748.5 mm., m.p. 49—50.5° (benzoate, m.p. 44—45°; *o*-chlorobenzoate, b.p. 175—178°/2 mm.; α -naphthylcarbamate, m.p. 122—123°); γ -*p*-hydroxyphenyl- γ -ethylpentane (from C₂H₅·OH), b.p. 120—122°/4 mm., 275°/749.5 mm., m.p. 75.5—76.5° (benzoate, m.p. 74—75°; *o*-chlorobenzoate, m.p. 67—68°; α -naphthylcarbamate, m.p. 133—135°); β -*p*-hydroxyphenyl- β - γ -trimethylbutane [from CMe₂Bu·OH (prep. from COMeBu and MgMeI)], b.p. 287°/748.5 mm., m.p. 133—134° (benzoate, m.p. 84—84.5°; *o*-chlorobenzoate, m.p. 83—85°). The above phenols are also prepared (diazo-method) from the corresponding *p*-aminophenyl derivatives, b.p. 117—118°/5 mm., 145—146°/10 mm., 124—125°/5 mm., 146—148°/11 mm., 120—121°/5 mm., 128—131°/5 mm., and m.p. 55—56°, respectively, which are obtained by reduction of the respective *p*-nitrophenyl derivatives, b.p. 292°/741 mm., 291°/741 mm., 284°/741 mm., 285°/741 mm., 277°/741 mm., 282°/741 mm., and m.p. 108°, which are prepared by nitration of the appropriate CPhAlk₃ and are oxidised to *p*-NO₂·C₆H₄·CO₂H. H. B.

Copper compounds of *o*-aminophenol and its *N*-alkyl derivatives. F. HORN (J. pr. Chem., 1937, [ii], 149, 298—300).—Fehling's solution and *o*-NH₂-phenols give, but not quantitatively, the following ppts.: from *o*-NH₂·C₆H₄·OH C₁₂H₁₂O₂N₂Cu, amorphous, m.p. (+H₂O) 225—230° (decomp.), (anhyd.) 220—225° (decomp.); from *o*-NHMe·C₆H₄·OH C₁₄H₁₆O₂N₂Cu, amorphous, +2H₂O and anhyd., m.p. 160—165° (decomp.); from *o*-NMe₂·C₆H₄·OH C₁₆H₂₀O₂N₂Cu, m.p. 218—219° (decomp.); from *o*-NEt₂·C₆H₄·OH C₂₀H₂₈O₂N₂Cu, m.p. 216° (decomp.). The products are probably complex salts, since none are formed from the *m*- or *p*-isomerides (*p*-NH₂·C₆H₄·OH ppts. Cu₂O). They are used to separate the *o*-compounds from mixtures. *o*-Dimethylaminophenol *H* oxalate has m.p. 167—169° (decomp. 172°). R. S. C.

New aromatic fluorine derivatives. (MME.) H. DEGIORGI and E. V. ZAPPI (Bull. Soc. chim., 1937, [v], 4, 1636—1642; cf. A., 1936, 1374).—5-Nitro-*m*-anisidine (improved prep.) is converted into 5-nitroanisole-3-diazonium borofluoride, m.p. 150° (decomp.), and thence into 5-fluoro-3-nitroanisole (I), which (Sn-HCl) yields 5-fluoro-*m*-anisidine sulphate (+2H₂O) [reconverted by diazotisation etc. into (I)]. Hydrolysis of (I) gives 5-fluoro-3-nitrophenol (II), m.p. 112° [methylated to (I)]. 3:5-Dinitrophenetole (improved prep.) is reduced (Na₂S) to 5-nitro-*m*-phenetidine, from which 5-nitrophenetole-3-diazonium borofluoride, decomp. 110°, is obtained, and thence 5-fluoro-3-nitrophenetole, m.p. 63.5—64°, hydrolysed to (II). 3:5:1-(NO₂)₃C₆H₃·NH₂, from the azide (cf. A., 1934, 1343), is converted into 3:5-dinitrobenzene-1-diazonium borofluoride, decomp. 203°, and into 5-fluoro-*m*-dinitrobenzene, m.p. 43°, reduced (NH₄SH) to 5-fluoro-*m*-nitroaniline, m.p. 115—116° (converted into *m*-C₆H₄·F·NO₂). E. W. W.

Compounds of phenyl *p*-nitrophenyl sulphide and ether with sulphuric acid. Example of thioquinonoid formation. H. H. HODGSON and

R. SMITH (J.C.S., 1937, 1634—1637).—F.p. measurements show the existence of 2:1 and 1:1 compounds, f.p. 51.7° and 50.3°, respectively, of *p*-NO₂·C₆H₄·SPh (I) and H₂SO₄ and of a 1:1 compound, m.p. 51.8°, of *p*-NO₂·C₆H₄·OPh (II) and H₂SO₄. Quinonoid structures, involving O^{IV} and S^{IV}, are postulated for these compounds; the formation by (I) of the acid salt shows it to be more strongly basic than (II). The compounds decompose when heated for some time. Some double mols. are formed in solution in the org. ingredient, but not in H₂SO₄. R. S. C.

Estrogenic substance from the demethylation of anethole. A. SERINI and K. STEINRUCK (Naturwiss., 1937, 25, 682—683).—Demethylation of anethole by MgEtI yields, in addition to hydroxypropenylbenzene, a substance (I) (Ac₂ derivative, C₂₆H₃₄O₄, m.p. 186°); demethylation by MgPrⁱI yields the homologue (Ac₂ derivative, C₂₈H₃₈O₄, m.p. 175°) of (I). Both Ac₂ derivatives are active (Allen-Doisy rat-unit 5—10 µg.); they are probably [*p*-OAc·C₆H₄·CH(CHMeR)·]₂ (R = Et or Prⁱ) (cf. Dodds and Lawson, A., 1937, II, 229, 361). F. O. H.

New form of resorcinol.—See A., I, 502.

Phase diagrams of binary systems of guaiacol and amines and of benzylamine with phenols. N. A. PUSHIN and I. I. RIKOVSKI (Annalen, 1937, 532, 294—299).—Guaiacol exists in an α -modification stable between 30° and -3.5° and a β -form stable below -3.5°. In the cryst. condition it does not form definite compounds or solid solutions with C₆H₆ or NPhMe₂ although it gives an equimol. compound with NH₂Ph. It forms compounds with quinoline (1:1), m.p. 12°, NHPH·NH₂ (1:2), m.p. 16°, and piperidine (2:1), m.p. 76°. Thermal analysis shows that NH₂·CH₂Ph gives compounds with PhOH (1:1), m.p. 22.0°, and (1:3), m.p. 15.3°, *o*-cresol (1:1), m.p. 7.5°, *m*-cresol (1:1), m.p. 36.4°, *p*-cresol (1:1), m.p. -6°, and (1:3), m.p. 20°, *o*-C₆H₄Cl·OH (1:1), m.p. 47.5°, and (1:3), m.p. 55°, *p*-C₆H₄Cl·OH (1:1), m.p. 16°, and (1:3), m.p. 55°, and guaiacol (1:1), m.p. 15.5°, and (1:3), m.p. 32°. H. W.

Synthesis of 3-iodoveratrole. F. MAUTHNER (J. pr. Chem., 1937, [ii], 149, 328—329).—Veratrole-3-carboxylic acid gives successively the chloride (by PCl₅) and amide, m.p. 93—94°, 3-amino- (by NaOCl), b.p. 136—138°/15 mm., and 3-iodo-veratrole, m.p. 45—46°, b.p. 144—145°/14 mm. R. S. C.

Trinitrophenoroglucinol. F. ŠORM and Z. DRÁPALOVÁ (Chem. Obzor, 1937, 12, 153—156).—By boiling 1:3:5-trichloro-2:4:6-trinitrobenzene (I) with a dil. (3%) aq. EtOH solution of excess of alkali hydroxide, a 55% yield of the normal alkali salt of trinitrophenoroglucinol (II) was obtained. (I) was converted by a boiling aq. EtOH solution of NH₃ into 1:3:5-trinitro-2:4:6-triaminobenzene, converted by boiling with aq. NaOH into the normal Na salt of (II) in 70% yield. The preps. of the normal K, NH₄, Li, Ba, Sr, Ca, Cd, Pb, and Ag salts of (II) are described. F. R.

Esterification of alcohols. W. HÜCKEL, F. NERDEL, and F. REIMER (J. pr. Chem., 1937, [ii], 149, 311—316).—By partial reaction with COCl₂-

$C_5H_5N-Et_2O$ *trans*-decahydro- β -naphthol, m.p. 53° (carbonates, m.p. 99° and 92°), is freed from its more reactive isomeride, m.p. 75° (carbonates, m.p. 119° and 78–79°). *trans*-2-Hydrindanol is shown to be a racemate by formation of carbonates, m.p. 73–74° and 52–56°. *p*-Nitrobenzoates are not readily obtained from *tert.* alcohols, except from alcohols, $CRMe_2 \cdot OH$. The following *p*-nitrobenzoates are described: Bu^r , m.p. 115–117°, cyclohexyldimethylcarbinyl, m.p. 101–103°, and 1-propyl-1-cyclohexyl (poor yield), m.p. 46–48°. Camphene hydrate, 1-isopropylcyclohexan-1-ol, and *trans*-2-methyldecahydro-2-naphthol, m.p. 92–93° (*p*-nitrobenzoate, m.p. 112–114°, prepared by K in PhMe), do not react with $p-NO_2 \cdot C_6H_4 \cdot COCl$ in C_5H_5N . R. S. C.

Preparation of *p*-phenyltriphenylcarbinol and existence of a metastable form. D. B. CLAPP and A. A. MORTON (J. Amer. Chem. Soc., 1937, 59, 2074–2075).— $p-C_6H_4PhCl$ (0.8 mol.), $COPh_2$ (0.8 mol.), and Na powder (0.2 mol.) in C_6H_6 give 67% of *p*-phenyltriphenylcarbinol, m.p. (stable) 135–136°; the first prep. gave a metastable form, m.p. 112–113°. H. B.

Preparation and pyrolysis of triphenylmethyl ethers of complex function. C. D. HURD and E. M. FILACHIONE (J. Amer. Chem. Soc., 1937, 59, 1949–1952).—*Et* α -triphenylmethoxypropionate, m.p. 79–80°, decomposes in the anticipated manner at 300° (bath) in N_2 , forming $AcCO_2Et$ (71%) and $CHPh_3$ (74%). $CPh_3 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, m.p. 102–103° (lit. 98–100°), undergoes disproportionation at 140–145°/6 mm. or atm. pressure to $(CH_2 \cdot OH)_2$ and $(CH_2 \cdot O \cdot CPh_3)_2$ (I), and is formed when (I) is heated with an excess of $(CH_2 \cdot OH)_2$. Decomp. of (I) at 340–350° (bath) gives $CHPh_3$ (61%), $COPh_2$, CH_2O , and CO; $(CHO)_2$ or $CPh_3 \cdot O \cdot CH_2 \cdot CHO$ may have been formed and undergone further decomp. α -Triphenylmethoxy- β -ethoxyethane, m.p. 77–78°, at 325–330° (bath) affords $CHPh_3$, $COPh_2$, $MeCHO$, $OEt \cdot CH_2 \cdot CH_2 \cdot OH$, and $(CH_2 \cdot OEt)_2$. α -Ethylideneglycerol CPh_3 ether has m.p. 105–106°. The above CPh_3 ethers are prepared from the OH-compounds and CPh_3Cl in C_5H_5N . H. B.

Action of magnesium phenyl bromide on chloroacetyl chloride and related compounds. J. S. W. BOYLE, A. MCKENZIE, and W. MITCHELL (Ber., 1937, 70, [B], 2153–2160).—Addition of $CHPhCl \cdot COCl$ to $MgPhBr$ in Et_2O gives $\alpha\beta\beta$ -tetraphenylethanol, m.p. 232.5–233° [identical with the product obtained from $MgPhBr$ and phenyldeoxybenzoin (I)], and resin, whereas (I) results when the order of admixture of the reactants is reversed. $CH_2Cl \cdot COCl$ and $MgPhBr$ give $\alpha\beta\beta$ -triphenylethanol, m.p. 87.5–88.5°, and *as*-diphenylchlorohydrin, m.p. 66°. $\alpha\beta\beta$ -Triphenylethylene glycol, m.p. 163°, is derived from $CHCl_2 \cdot CO_2H$ and $MgPhBr$. *r*- $\gamma\gamma\gamma$ -Trichloro- β -hydroxybutyric acid or its *Et* ester and $MgPhBr$ afford *r*- $\alpha\gamma$ -dihydroxy- $\alpha\alpha$ -diphenyl- γ -trichloromethylpropane, m.p. 178.5°, converted by boiling 2N-NaOH into $\alpha\gamma$ -dihydroxy- $\gamma\gamma$ -diphenyl-*n*-butyrolactone, m.p. 110°. *Me* (–)- $\gamma\gamma\gamma$ -trichloro- β -hydroxybutyrate, m.p. 62.5–63°, $[\alpha]_D -33^\circ$ in $EtOH$, or the corresponding acid do not give cryst. compounds with

$MgPhBr$. Definite compounds could not be obtained from $MgPhBr$ and dimethylmalic ester. H. W.

Derivatives of cyclo-pentane- and -hexane-1:2-diols. M. MOUSSERON and R. GRANGER (Compt. rend., 1937, 205, 327–329).—Addition of Cl_2 and Br to cyclohexene affords only *trans*-1:2-dichloro- (I), b.p. 75°/15 mm. and -1:2-dibromocyclohexane, respectively, identical with the products obtained by interaction of 2-chloro- (II) and 2-bromocyclohexanol (III) with PCl_5 and PBr_3 . 1-Methyl- Δ^3 -cyclohexene having $[\alpha]_D +110^\circ$ affords with Br two isomeric forms, b.p. 105°/15 mm. and 108°/15 mm., of 3:4-dibromo-1-methylcyclohexane. (II) with PBr_3 or (III) with PCl_5 affords 1-chloro-2-bromocyclohexane, b.p. 94°/17 mm. *trans*- (II) when heated with HCl affords some of the *cis*-isomeride. Prolonged interaction of (II) with a hot solution of NaOAlk affords 2-alkyloxycyclohexanol. The following are similarly prepared (b.p. at 760 mm.): 2-methoxy-, b.p. 175°, and 2-ethoxy-cyclopentanol, b.p. 182°; 2-propoxy-, b.p. 205°, 2-cyclohexoxy-, m.p. 50°, 2-methoxy-1-methyl-, b.p. 181°, and -1-ethylcyclohexanol, b.p. 186°. 1:2-Dibromocyclohexanes when heated with conc. $EtOH-KOH$ or NaOAlk afford the corresponding 1:2-di-ethers. The following are prepared (b.p. at 760 mm.): 1:2-dimethoxy-, b.p. 108°, and 1:2-diethoxy-cyclopentane, b.p. 126°; 1:2-diethoxy-, b.p. 151°, 1:2-dipropoxy-, b.p. 159°, 1:2-diisopropoxy-, b.p. 160°, 1:2-dibutoxy-, b.p. 192°, and 1:2-dicyclohexoxy-cyclohexane, b.p. 120°/15 mm. The above mono- and di-ethers of cyclohexanediol with PBr_3 afford 1:2-dibromocyclohexane. Oxidation (CrO_3) of 2-alkyloxy-cyclopentanol and -cyclohexanol affords 2-alkoxy-cyclopentanone and -cyclohexanone, respectively. The following are prepared (b.p. at 750 mm.): 2-methoxy-, b.p. 179°, and 2-ethoxy-cyclopentanone, b.p. 186°, and 2-propoxycyclohexanone, b.p. 209°.

J. L. D.

Derivatives of phenyl- and *s*-diphenyl-ethylene glycol. L. PALFRAY and R. PANNELIER (Bull. Soc. chim., 1937, [v], 4, 1913–1916).—Phenylethylene glycol (*bisphenylurethane*, m.p. 148°) with aliphanyl chloride in C_6H_6 yields a *mono*-, m.p. 168°, and *di*-allophanate, m.p. 240–241°; hydrobenzoin similarly yields a *di*-allophanate, m.p. 280°, but does not react with $PhNCO$.

J. D. R.

Manufacture of diamino-alcohols of the aromatic series.—See B., 1937, 1024.

Sterols. XIX. *epi*Ergosterol and *epi*- α -ergosterol. R. E. MARKER, O. KAMM, J. F. LAUCIUS, and T. S. OAKWOOD (J. Amer. Chem. Soc., 1937, 59, 1840–1841).—Ergostatrienone (Oppenauer, A., 1937, II, 250) is reduced $[Al(OPr^i)_3]$ in Pr^iOH followed by $MeOH-KOH$ to ergosterol and *epiergosterol* (I), m.p. 152°, $[\alpha]_D^{25} +50^\circ$ in $CHCl_3$ (acetate, m.p. 126°). (I), which is not pptd. by digitonin, and is not identical with lumisterol. α -Ergosterone [from α -ergosterol (II) and Cu powder at 250°/4 mm.] is similarly reduced to (II) and *epi*- α -ergosterol, m.p. 188.5°, $[\alpha]_D^{25} +5.3^\circ$ in $CHCl_3$ (acetate, m.p. 119.5°). H. B.

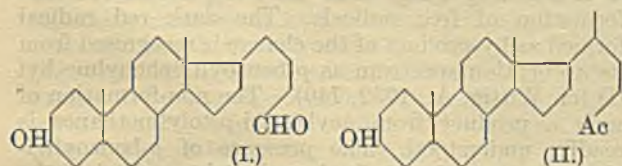
Fission of sterol digitonides and other molecular compounds by distillation in high vacuum.

A. VON CHRISTIANI and M. PAILER (Mikrochim. Acta, 1937, 1, 26—29).—Cholesterol, coprosterol, etc. from the digitonides, and $C_{10}H_8$, indene, etc. from the picrates, may be recovered in pure form in 70—90% yield by heating the mol. compounds at 100—250° in a high vac. J. S. A.

Polyterpenes and polyterpenoids. CXVII. Conditions and mechanism of the dehydrogenation of homologous sterols and of cholic acid. L. RUZICKA and M. W. GOLDBERG (Helv. Chim. Acta, 1937, 20, 1245—1253).—If possible, the temp. of dehydrogenation of cholesterol (I) or cholic acid (II) should be $\geq 350^\circ$ if the formation of chrysene is to be avoided and the primary products are to be isolated (cf. Diels *et al.*, A., 1927, 241, 1930, 470; Ruzicka *et al.*, A., 1933, 820). Further examination shows that the main product of the dehydrogenation of ergosterol (III) with Se according to the older or newer conditions of Diels (A., 1930, 470; 1937, II, 95) is the hydrocarbon $C_{26}H_{26(24)}$, fractionation of which appears impossible by methods dependent on solubility or volatility. Re-examination confirms the homogeneity of the hydrocarbon, m.p. 205—206°, obtained by dehydrogenation of phytosterol (IV); analyses thereof and of the ketone, m.p. 204—204.5°, derived therefrom favour the respective formulæ $C_{27}H_{26}$ and $C_{27}H_{24}O$. At a temp. $\geq 350^\circ$, therefore, dehydrogenation of (II) C_{24} , (I) C_{27} , (III) C_{28} , and (IV) C_{29} occurs with loss of 2 C and formation of a fifth ring from the long side-chain. These hydrocarbons probably represent a homologous series and have almost identical absorption spectra. Since the product $C_{22}H_{16}$ from (II) is methyl-naphthofluorene it is probable that this or a very similar ring system is present in the other hydrocarbons. The distribution of the side-chains is unknown but must be such that a place is available in the aromatic ring system for the Me and Et group of the more complex sterols.

H. W.

Sex hormones. XXV. Oxidation of saturated sterol derivatives with chromium trioxide. L. RUZICKA, M. OBERLIN, H. WIRZ, and J. MEYER (Helv. Chim. Acta, 1937, 20, 1283—1290).—The mother-liquors obtained after removal of androsterone acetate semicarbazone from the products of the oxidation of epicholestanyl acetate by CrO_3 in AcOH at about 90° (A., 1934, 1221) yield the semicarbazone, m.p. 224.5—225.5°, of 3-epiacetoxyallocholanaldehyde (I); the structure of the compound



is rendered probable by the co-formation of the corresponding acid in considerable amount. In addition, the semicarbazone, m.p. 221—223°, of epinorcholestan-3-ol-25-one (II) is obtained, produced in much larger proportion when the oxidation is effected at 25—30°. (II) has m.p. 181—182.5° (corr.), and yields an acetate (III), m.p. 111° (corr.). Oxidation of (II) with CrO_3 in AcOH affords the

diketone, $C_{26}H_{42}O_2$, m.p. 139.5—140.5° (corr.). Condensation of (III) with a large excess of $MgMeI$ followed by hydrolysis affords 25-hydroxycholestanol, m.p. 191—193° (corr.), transformed by Ac_2O in C_5H_5N into the monoacetate, m.p. 154° (corr.). (III) with $PhCHO$ and HCl in $AcOH$ gives the non-cryst. $:CHPh$ derivative, which is oxidised by CrO_3 in $AcOH$ and then hydrolysed to 3-epihydroxyallocholic acid, m.p. 218—220° (corr.) [Me ester, m.p. 166—168° (corr.)]. H. W.

Vitamin- D_4 .—See A., III, 327.

Phytosterol, $C_{28}H_{47}OH$, and ketone, $C_{31}H_{52}O$, from *Citrus grandis*.—See A., III, 244.

Cumotocopherol, $C_{28}H_{48}O_2$, and its allophanate, m.p. 146°, $[\alpha]_D^{25} + 6.7^\circ$ in $CHCl_3$.—See A., III, 497.

Pregnane-3 : 17 : 20-triol, m.p. 243—244°, and its diacetate, m.p. 136.5°.—See A., III, 361.

Absorption spectra of compounds related to sterols. —See A., II, 494.

Tertiary alcohols of the cyclopentanopolyhydrophenanthrene series. —See B., 1937, 1135.

Synthesis of 9 : 10-dihydroxy-5-phenyl-9 : 10-dialkyl-9 : 10-dihydro-1 : 2-benzanthracenes and related compounds. W. E. BACHMANN and J. T. BRADBURY (J. Org. Chem., 1937, 2, 175—182).—1 : 2-Benzanthraquinone and $MgMeI$ or $MgEtBr$ give 9 : 10-dihydroxy-9 : 10-dimethyl-, m.p. 181.5—182.5°, and -9 : 10-diethyl-9 : 10-dihydro-1 : 2-benzanthracene, m.p. 145—145.5°. The Et_2 , but not the Me_2 , compound has oestrogenic activity. With $MgPr^aBr$, a substance, $C_{21}H_{18}O_2$, m.p. 91—94°, is obtained. 5-Keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene [from β -(3-phenanthroyl)propionic acid, obtained by the Friedel-Crafts reaction from phenanthrene and succinic anhydride, together with β -(2-phenanthroyl)propionic acid, new m.p. 207—208°; cf. A., 1933, 1043] and $MgPhBr$ give 5-hydroxy-5-phenyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene, m.p. 157—159°, dehydrated ($KHSO_4$) to 5-phenyl-7 : 8-dihydro-1 : 2-benzanthracene, m.p. 125—126°, dehydrogenated (S; Cu) to 5-phenyl-1 : 2-benzanthracene, m.p. 151—152° (picrate, m.p. 165—166°). This is oxidised ($Na_2Cr_2O_7$ -AcOH) to 5-phenyl-1 : 2-benzanthraquinone, m.p. 189—189.5°, from which $MgMeI$, $MgEtBr$, and $MgPr^aBr$ give respectively 9 : 10-dihydroxy-5-phenyl-9 : 10-dimethyl-, m.p. 160—164° (cis + trans?) recryst. to a product, m.p. 130°, resolidifying to remelt at 215—216°, -9 : 10-diethyl- (I), m.p. 147.5—148°, and -9 : 10-di-n-propyl-9 : 10-dihydro-1 : 2-benzanthracene (II), m.p. 191.5—192.5°. Both (I) and (II) are oestrogenic. $MgPhBr$ gives a mixture containing small quantities of the 9 : 10-diphenyl compound (?), m.p. 240° (decomp.), with Ph_2 . E. W. W.

Constitution of natural phenolic resins. IX. Structure of lariciresinol. Preliminary experiments on the synthesis of lignandiols. R. D. HAWORTH and W. KELLY (J.C.S., 1937, 1645—1649).—Structures assigned (A., 1937, II, 202) to lariciresinol (I) and isolariciresinol (II) are confirmed. Lignan is adopted as a generic name for substances of bisconiferyl structure. Unsuccessful attempts to

synthesise lignandiols and successful syntheses of aryltetronic acids are described. Anhydroisolaricresinol Me_2 ether is unaffected under conditions causing the change of (I) into (II); with $\text{Pb}(\text{OAc})_4$ at $70-80^\circ$ it gives *dehydroanhydroisolaricresinol Me₂ ether*, m.p. $201-202^\circ$. The Me_2 ether of (I) gives *laricresinol CPh₃ ether Me₂ ether*, m.p. 134° , converted by $80\% \text{HCO}_2\text{H}$ into the $(\text{HCO})_2$ derivative, m.p. $102-103^\circ$, of isolaricresinol Me_2 ether. $\text{CH}_2\text{Bz}\cdot\text{CHBz}\cdot\text{CO}_2\text{Et}$ and $(\text{CHBz}\cdot\text{CO}_2\text{Et})_2$ do not condense with CH_2O , HCO_2Et , or $\text{Et}_2\text{C}_2\text{O}_4$; the former ester with alkali gives $\text{CH} \begin{smallmatrix} \text{CPh}\cdot\text{O} \\ \text{CBz}\cdot\text{CO} \end{smallmatrix}$; the latter ester with CH_2O and alkali gives BzOH , and with conc. H_2SO_4 gives Et_2 2:5-diphenylfuran-3:4-dicarboxylate, which resists reduction. *Et* $\alpha\beta$ -diveratroylpropionate [from α -bromoacetoveratrone and $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$], m.p. $110-111^\circ$, with $10\% \text{KOH}-\text{MeOH}$ gives the lactone, m.p. $155-156^\circ$, of γ -hydroxy- α -veratroyl- γ -3:4-dimethoxyphenyl- Δ^8 -butenoic acid (*K* salt), or, when $0.1\text{N}-\text{NaOH}$ is dropped into its boiling solution in aq. MeOH , affords $\alpha\beta$ -diveratroylethane, m.p. $180-181^\circ$, converted by $\text{HCl}-\text{MeOH}$ into 2:5-di-3':4'-dimethoxyphenylfuran, m.p. $154-155^\circ$ (no FeCl_3 colour), insol. in NaOH . $\text{Et}_2\text{C}_2\text{O}_4$ and acetoveratrone (III) give *Et veratroylpyruvate*, m.p. $104-105^\circ$ [corresponding acid, m.p. $192-193^\circ$ (decomp.)], which does not react with $\text{CH}_2(\text{CO}_2\text{Et})_2$, $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, or $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$; (III), veratroylacetoneitrile, and $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ are similarly unreactive. α -Veratroyl- β -3:4-dimethoxybenzylbutyrolactone with CH_2O in cold $2\% \text{NaOH}$ gives veratric acid and an oil, but with hot $2\% \text{NaOH}$ yields γ -veratroyl- γ -3:4-dimethoxyphenylisobutyl alcohol (IV), m.p. $98-99^\circ$, which with $\text{HCl}-\text{AcOH}$ (not $-\text{MeOH}$) affords 6:7-dimethoxy-4-3':4'-dimethoxyphenyl-2-chloromethyl-1:2-dihydronaphthalene, m.p. $108-109^\circ$, converted by hot $5\% \text{KOH}-\text{MeOH}$ into (?) 6:7-dimethoxy-1-3':4'-dimethoxyphenyl-3-methylnaphthalene, m.p. 140° , sublimates at $200-220^\circ$ (bath)/ 0.1 mm. CH_2O reacts with (IV) in presence of alkali, but gives indefinite products. The $(\text{CH}_2\text{O})_2$ -analogue, m.p. $103-104^\circ$ (oxime, m.p. $139-140^\circ$), of (IV) is prepared. β -Keto- α -cyano- γ -p-nitrophenoxypropylbenzene, m.p. $156-157^\circ$, is obtained only in poor yield from $\text{CH}_2\text{Ph}\cdot\text{CN}$ and $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$. β -Keto- α -cyano- γ -benzyloxypropylbenzene (obtained readily from $\text{CH}_2\text{Ph}\cdot\text{CN}$ and $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Me}$), m.p. $72-73^\circ$, with $\text{HCl}-\text{MeOH}$ gives phenyltetronic acid, converted by H_2O at 200° in poor yield into $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$. 4- β -Keto- α -cyano- γ -benzyloxypropyl-3:4-dimethoxy-, m.p. $78-79^\circ$, and -3:4-methylenedioxy-benzene, m.p. $72-73^\circ$, and 3:4-dimethoxy-, m.p. $211-213^\circ$, and -methylenedioxy-phenyltetronic acid, m.p. 268° (decomp.), are similarly prepared. R. S. C.

Direct synthesis of dihydroislauronic and islauronic acids. P. C. GUHA and K. S. SUBRAHMANYAN (Current Sci., 1937, 6, 94-95).— $\text{CMe}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ with $\text{CO}_2\text{Et}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and Zn gives *Et* β -hydroxy- β' -carbethoxy- $\alpha\alpha\beta$ -trimethyl-adipate (acid, m.p. $165-166^\circ$) and *Et* γ -carbethoxy- $\alpha\alpha\beta$ -trimethyl- Δ^8 -butene- $\alpha\delta$ -dicarboxylate, b.p. $155-162^\circ/5 \text{ mm.}$ (acid, m.p. $239-240^\circ$; triamylide, m.p. 235° ; anilide anil, m.p. 212°), which with Na yields

enolic *Et* 1:1:2-trimethyl- Δ^2 -cyclopenten-5-one-3:4-dicarboxylate, b.p. $125-128^\circ/3 \text{ mm.}$, hydrolysed to the -3-carboxylic acid, m.p. $186-187^\circ$ (oxime, m.p. $139-140^\circ$; semicarbazone, m.p. 225°), which on Clemmensen reduction gives dihydroislauronic acid. F. R. G.

Reformatsky reaction with benzamide. A. BANCHETTI (Atti R. Accad. Lincei, 1937, [vi], 25, 485-488).— NH_2Bz , Zn , and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ give a product which after treatment with H_2SO_4 gives BzOH and resins, but no $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, or $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$. If the product is not acidified, but extracted with (damp) Et_2O , a substance $(\text{NH}_2\text{Bz})_2\cdot\text{ZnBr}_2$ (I), m.p. $157-158^\circ$, is obtained. It is suggested that a compound $\text{BrZn}\cdot\text{NH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ is formed, and converted by H_2O into (I), ZnO , and EtOAc . E. W. W.

Preparation of 2:4-dinitro-benzonitrile and -benzoic acid. F. R. STORRIE (J.C.S., 1937, 1746).—Prep. of these substances is improved [85% and 95% yield, respectively, from $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}_2$]. R. S. C.

Thermal decomposition of dibenzoyl peroxide in presence of deuterium. H. ERLÉNMEYER and W. SCHOENAUER (Helv. Chim. Acta, 1937, 20, 1015-1016).—The reaction gives Ph_2 free from D, indicating the improbability of the intermediate production of free radicals. H. W.

[Attempted] synthesis of acyloins. K. BERNHAUER and R. HOFFMANN (J. pr. Chem., 1937, [ii], 149, 317-320).—Unsaturated esters do not give acyloins with Na in xylene etc. $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ is mainly resinified. *Et* α -cyclogeranate gives a poor yield of a substance, m.p. $112-113^\circ$. $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{R}$ ($\text{R} = \text{Me}$, Et , Bu , or CH_2Ph) gives a ketone, $\text{C}_{16}\text{H}_{16}\text{O}$, m.p. 176° (*p*-nitrophenylhydrazones, m.p. 222° ; semicarbazone, m.p. $164-165^\circ$; oxidised to BzOH ; reduced by $\text{Zn}-\text{HCl}$ to a substance, $\text{C}_{16}\text{H}_{18}$, m.p. $64-65^\circ$), and a small amount of a ketone, m.p. $108-110^\circ$. R. S. C.

Occurrence of free radicals in chemical reactions. IX. A. Thermal decomposition of acylazotriphenylmethanes. B. Mode of reaction of diacyl peroxides. H. WIELAND, T. PLOETZ, and H. INDEST (Annalen, 1937, 532, 166-190; cf. A., 1934, 1215; 1935, 77).—A. Thermal decomp. of acylazotriphenylmethanes occurs mainly, $\text{R}\cdot\text{CO}\cdot\text{N}_2\cdot\text{CPh}_3 \rightarrow \text{R}\cdot\text{CO}\cdot\text{CPh}_3 + \text{N}_2$, and is independent of the formation of free radicals. The dark red radical formed as by-product of the change is recognised from its absorption spectrum as *p*-benzoyltriphenylmethyl (I) (cf. Wittig, A., 1932, 746). The non-formation of such a product from acylazotri-*p*-tolylmethanes is readily understood. The presence of *p*-benzoyltriphenylmethane in the final product is ascribed to the hydrogenation of (I) by some unknown agent. The radical is the primary product, but this does not arise immediately from the N_2 compound since, under favourable circumstances, evolution of N_2 ceases before the red colour commences to develop. The red radical is decolorised by the N_2 compound in the act of its decomp.—not by the substance itself—since it also disappears when the N_2 compound is

decomposed by heat in its solution. The exact agent has not been identified, but it cannot be CPh_3 . The radical not only appears in the free state after complete decomp. of the N_2 compound, but is present in latent form in the reaction solution, but not as dimeric ethane. If the radical is removed by O_2 the solution remains pale; addition of CPh_3 causes rapid liberation of the free radical and CPh_3 is simultaneously utilised. The form of union of the acyltriphenylmethyl is not obvious. It is also liberated by NH_2Ph , NH_3 , and other bases, and considerable possibility of a nitrogenous intermediate exists. This is supported by the observation that evolution of N is never quant. and part remains as a substituted hydrazine. The change can therefore be: $\text{R}\cdot\text{CO}\cdot\text{N}_2\cdot\text{CPh}_3 \rightarrow \text{R}\cdot\text{CO}\cdot\text{N}\cdot\text{N}\cdot + \text{CPh}_3$. Explosive decomp. of acylazo-compounds (without solvent) is accompanied by production of small amounts of the aldehyde corresponding with the acyl residue; this is never formed during the regulated decomp. *Triphenylmethylpyridine*, m.p. 264—267° (hydrochloride), *benzoylazotri-p-tolylmethane*, *formylazotriphenylmethane*, m.p. 156—157°, *benzoylazo-p-benzoyltriphenylmethane*, *benzoyl-p-benzoyltriphenylmethane*, m.p. 142°, and the compound, $\text{C}_{30}\text{H}_{30}\text{O}_2$, m.p. 212°, are incidentally described.

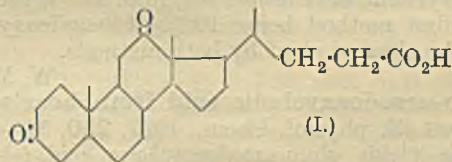
B. The decomp. of further diacyl peroxides is investigated. *Bz* α -naphthoyl peroxide, m.p. 67°, from $\alpha\text{-C}_{10}\text{H}_7\cdot\text{COCl}$ and NaO_2Bz in aq. COMe_2 at 0°, when heated in admixture with sand, gives some CO_2 and BzOH . The neutral product is hydrolysed to BzOH , $\alpha\text{-C}_{10}\text{H}_7\cdot\text{COCl}$, some PhOH and higher phenols, naphtholcarboxylic acids, and more complex acids which give sparingly sol. Na salts. *Bz* phenylacetyl peroxide, m.p. 35.5° (decomp.), decomposes very readily and almost quantitatively into CO_2 and $\text{CH}_2\text{Ph}\cdot\text{OBz}$, whereas with $\text{BzO}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ change occurs only at 80° and is accompanied by side reactions. This influence of Ph renders understandable the failure to prepare $(\text{CHPh}_2\cdot\text{CO})_2\text{O}_2$, $\text{BzO}_2\cdot\text{CHPh}_2$, or $(\text{CPh}_3\cdot\text{CO})_2\text{O}_2$. Thermal decomp. of Bz_2O_2 in CHPh_3 at 100° gives $\text{CPh}_3\cdot\text{OBz}$, BzOH , C_6H_6 , and sometimes $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$, the changes being explained, $\text{Bz}_2\text{O}_2 + \text{CHPh}_3 \rightarrow \text{BzOH} + \text{CPh}_3\cdot\text{OBz}$ and $\text{Bz}_2\text{O}_2 + \text{CHPh}_3 \rightarrow \text{CPh}_3\cdot\text{OBz} + \text{CO}_2 + \text{C}_6\text{H}_6$. Bz_2O_2 and CPh_3 , whether obtained in the usual manner or from specially purified CPh_3Cl and Hg , give much lower yields of CPh_4 than those claimed by Medvedev and Alexeeva (A., 1932, 379). The main products are $\text{CPh}_3\cdot\text{OBz}$ and BzOH ; COPh_2 does not appear. CPh_4 is accompanied by an inseparable mixture of hydrocarbons. The possibility that the fourth Ph is yielded by Bz_2O_2 is rendered improbable by the small amount of CO_2 evolved and is excluded by the observation that CPh_4 also results when $(p\text{-C}_6\text{H}_4\text{Ph})_2\text{O}_2$ is used. It therefore arises from C_6H_6 probably according to $\text{Bz}_2\text{O}_2 + \text{CPh}_3 \rightarrow \text{CPh}_3\cdot\text{OBz} + \text{PhCO}_2$; $\text{PhCO}_2 + \text{C}_6\text{H}_6 \rightarrow \text{BzOH} + \text{Ph}$; $\text{Ph} + \text{CPh}_3 \rightarrow \text{CPh}_4$. Et_2O does not appear to react with CPh_3 . H. W.

Iodonitrotyrosine. R. ZEYNEK (Biochem. Z., 1937, 293, 432—434).—3-Nitrotyrosine when treated with HIO_3 and HI gives an *iodonitrotyrosine*, m.p. 220° (decomp.), $\alpha_D + 10$ —11° in 4% HCl , in which the I is *ortho* to the OH . P. W. C.

New synthesis of caronic acid. R. GHOSH (J. Indian Chem. Soc., 1937, 14, 449—451).— $\text{CHNa}(\text{CO}_2\text{Et})_2$ and $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$ give *Et*₃ 2:2-dimethylcyclopropane-1:1:3-tricarboxylate, b.p. 153°/9 mm., converted by $\text{KOH}\text{-EtOH}$ into *cis*- with a small amount of *trans*-caronic acid, and by HCl into terebic acid. E. W. W.

Unexpected complication in the replacement of a diazo-group. V. M. RODIONOV and A. M. FEDOROVA (Bull. Soc. chim., 1937, [v], 4, 1703—1707).—The *diazonium sulphate* from 3-aminophthalic acid gives with MeOH at 40—50°, not 3-methoxyphthalic acid, but *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. *o*-Carboxybenzenediazonium sulphate [obtained using $n\text{-C}_5\text{H}_{11}\cdot\text{O}\cdot\text{NO}$] with MeOH gives *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ (and some BzOH and salicylic acid). 6-Carboxy-2:3-methoxybenzenediazonium chloride and 2-carboxy-3:4-dimethoxybenzenediazonium sulphate both yield 1:2:3- $\text{C}_6\text{H}_3(\text{OMe})_3$, accompanied respectively by *m*- and *o*-veratric acid. E. W. W.

Δ^4 :3:12-Diketocholeonic acid and its attempted transformation into 3:12-diketoallocholanolic acid. J. SAWLEWICZ and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 992—998).—4-Bromo-3:12-diketocholeonic acid is converted by boiling $\text{C}_5\text{H}_5\text{N}$ into Δ^4 :3:12-diketocholeonic acid (I), m.p. 199—201°, also obtained with acetoxy-3:12-diketocholeonic acid by means of KOAc . (I) and CH_2N_2 afford *Me*



Δ^4 :3:12-diketocholeonate (II), m.p. 154—155°. Hydrogenation (Raney Ni in MeOH) of (II) gives a product separated by digitonin into (after hydrolysis) α -3-hydroxy-12-ketocholeonic acid (oxidised deoxybilanic acid) and *Me* β -3-hydroxy-12-ketocholeonate, m.p. 126—128° (corr.); the corresponding acid, m.p. 224—225° (corr.), is oxidised to dehydrodeoxycholic acid. Hydrogenation of (II) with Pd and Pt successfully is described. H. W.

Δ^5 -3-Hydroxyætiucholeonic acid and its transformation products. M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 1040—1054).—Gradual addition of *Me* 3-hydroxybismnorecholenate in PhMe to MgPhBr in boiling Et_2O gives a *by-product*, m.p. about 165° (corr.; decomp.), and, mainly, *diphenyl- Δ^5 -3-hydroxyternorcholenylcarbinol*, m.p. 113° (corr.). The corresponding *monoacetate*, m.p. about 177° (corr.), and, after re-solidification, m.p. 188—189° (corr.), is transformed by boiling AcOH into α -*diphenyl- Δ^5 -acetoxycholenyl- β -methylethylene* (I), m.p. 221—222° (corr.), hydrolysed to the corresponding OH -compound, m.p. about 106° (corr.) after becoming opaque at about 85°. Bromination of (I) in CHCl_3 affords the *dibromide*, m.p. 171—174° (corr.), oxidised and then debrominated to Δ^5 -3-acetoxyætiucholeonic acid (II), m.p. 241—242° (corr.), $[\alpha]_D^{25} - 19.9^\circ$ in COMe_2 [*Me* ester, m.p. 153—154° (corr.)], a keto-fraction consisting chiefly of the acetates of pregnenolone and

trans-dehydroandrosterone, and a non-ketonic product, m.p. 171—173°. Δ^5 -3-Hydroxy α tiocholenic acid (III) [*Me* ester, m.p. 179—181° (corr.)] has m.p. 280—281° (corr.; decomp.). Hydrogenation (Pt in AcOH) of (II) affords β -3-acetoxy α tioallocholanolic acid, m.p. 247—249° (corr.), [*Me* ester, m.p. 142—144° (corr.)], hydrolysed to β -3-hydroxy α tioallocholanolic acid (IV), m.p. 256—258° (corr.) after becoming opaque at 145—150° [*Me* ester (V), m.p. 166—170° (corr.) or (as hydrate), m.p. about 90—100° and, after re-solidification, m.p. 166—170° (corr.)]. Oxidation of (IV) with CrO_3 in AcOH gives 3-keto α tioallocholanolic acid, m.p. 253—256° (corr.) [*Me* ester, m.p. 176—179°], reduced by Zn wool in HCl-AcOH to α tioallocholanolic acid, m.p. 229—231° (corr.). Bromination followed by oxidation and debromination of (III) gives Δ^4 -3-keto α tiocholenic acid, m.p. 236—242° (corr.), the *Me* ester, m.p. 130—131°, of which is hydrogenated (Pd followed by PtO_2) to (V) and *Me* α tiolithocholate, m.p. 143—144° (corr.). α tiolithocholic acid is oxidised by CrO_3 in AcOH to 3-keto α tiolithocholanolic acid, m.p. 246—249° (corr.) [*Me* ester, m.p. 147—149° (corr.)], reduced (Clemmensen) to α tiocholanolic acid.

H. W.

Synthesis of ursodeoxycholic acid. S. MIYAZI (Z. physiol. Chem., 1937, 250, 31—33; cf. Imai, A., 1937, II, 377).—3-Hydroxy-7-ketocholanolic acid in EtOH with NaOEt at 200° for 10 hr. or in AcOH containing 0.033% of conc. HCl with PtO_2 -H₂ gives ursodeoxycholic acid (*diformate*, m.p. 170°), the yield by the first method being 10%. Chenodeoxycholic acid is the chief product by both methods.

W. McC.

Glyco-ursodeoxycholic acid from bear's bile. S. MIYAZI (Z. physiol. Chem., 1937, 250, 34—36).—The bile yields glyco-ursodeoxycholic acid (+H₂O), m.p. 232°, $[\alpha]_D^{20} + 51.28^\circ$, converted by alkaline hydrolysis into glycine and ursodeoxycholic acid (I). An improved method of isolating (I), cholic and chenodeoxycholic acid from the bile is described.

W. McC.

Oxidation of cholic and deoxycholic acid with CrO_3 . Colour reaction of ketocholanolic acid with *m*-dinitrobenzene. K. KAZIRO and T. SHIMADA (Z. physiol. Chem., 1937, 249, 220—224).—Cholic acid in AcOH with aq. CrO_3 at 0° gives in 6—7 hr. a 65% yield of 3-hydroxy-7:12-diketocholanolic acid but no 3:12-dihydroxy-7-ketocholanolic acid. In the same way deoxycholic acid yields (much more slowly) 3-hydroxy-12-ketocholanolic acid and 7:12-dihydroxy-3-ketocholanolic acid yields dehydrocholic acid. Hence OH at C₍₁₂₎ is more easily oxidised than OH at C₍₃₎ and OH at C₍₇₎ than OH at C₍₁₂₎. Ketocholanolic acids having CO at C₍₃₎ (but not other ketocholanolic acids) give a violet colour with alkaline *m*-C₆H₄(NO₂)₂. (Cf. Zimmermann, A., 1935, 1032.)

W. McC.

Degradation of lithocholic acid to α tiolithocholic acid. J. SAWLEWICZ and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 949—953).—Addition of MgPhBr in Et₂O to *Me* bisnorlithocholate (Reindel and Niederlander, A., 1935, 1494) in boiling PhMe gives the non-cryst. diphenylcarbinol, which is treated with Ac₂O in C₅H₅N and then with boiling

AcOH; after chromatographic purification the product yields α -diphenyl-

β -3-acetoxy α tiocholyll- β -methylstyrene (I), m.p. 161—163° after softening at about 157°. (I) by CrO_3 in AcOH at 100° yields acetyl α tiolithocholic acid, m.p. 225—226° (corr.) (*Me* ester, m.p. 113—118°), hydrolysed to α tiolithocholic acid, m.p. 273—275° after becoming opaque at about 120°, $[\alpha]_D^{18} + 50^\circ \pm 2^\circ$ in dioxan [*Me* ester, m.p. 141—142° (corr.)].

H. W.

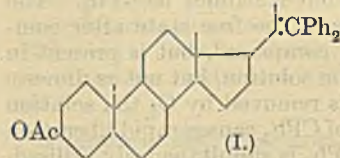
Condensation of succinic anhydride with the methyl ethers of dihydric phenols. G. A. DALAL and K. S. NARGUND (J. Indian Chem. Soc., 1937, 14, 406—410).—The condensation (AlCl_3) of $(\text{CH}_2\text{CO})_2\text{O}$ with the Me₁ and Me₂ ethers of dihydric phenols in PhNO₂, CS₂, and C₂H₅Cl₄ is described. The following substituted γ -keto- δ -phenylbutyric acids were prepared: 3:4- (*Me* ester, m.p. 90°, *Et* ester, m.p. 70°) and 2:4-dimethoxy- (*Et* ester, m.p. 70°; semicarbazone, m.p. 160°) [also synthesised from $(\text{CH}_2\text{CO})_2\text{O}$, 1:2:4-C₆H₃I(OMe)₂, and Mg]; 5-bromo-, m.p. 178°, and 5-nitro-2:4-dimethoxy-, m.p. 173°, 2-hydroxy-4-methoxy- (*Et* ester, m.p. 68°; semicarbazone, m.p. 175°), and 2:5-dimethoxy- (*Me* ester, m.p. 54°; *Et* ester, m.p. 46°; semicarbazone, m.p. 195°). Guaiacol and *p*-OH-C₆H₄-OMe do not condense.

A. Li.

Anisylmalonic acid and its derivatives. J. B. NIEDERL, R. T. ROTH, and A. A. PLENTL (J. Amer. Chem. Soc., 1937, 59, 1901—1903).—The following are prepared (usual methods) from *Et* α -cyano- α -anisylacetate, b.p. 152—153°/2 mm., which is obtained in 50—55% yield from *p*-OMe-C₆H₄-CH₂-CN, Et₂CO₃, and Na in Et₂O: anisylmalonic acid, m.p. 137—138° (*Et* H, m.p. 77—78°, and *Et*₂, b.p. 152—153°/2.5 mm., esters; diamide, m.p. 190—191°); *Et* α -cyano- α -anisyl-propionate, b.p. 136—138°/0.5 mm., and -butyrate, b.p. 142—143°/0.5 mm.; α -cyano- α -anisyl-acetamide, m.p. 144—145°, -propionamide, m.p. 143—144°, and -butyramide, m.p. 138°. *p*-C₆H₄Me-OMe with Na and CO₂ in amyl chloride (cf. Morton and Hechenbleikner, A., 1937, II, 101) gives 2:5-OMe-C₆H₃Me-CO₂H. *p*-OH-C₆H₄-CH(CO₂H)₂ (or derivatives) could not be obtained by direct condensation of CH₂(CO₂Et)₂ and PhOH or by rearrangement of OPh-CH(CO₂H)₂ (and its derivatives).

H. B.

Syntheses in the hydroaromatic series. II. Diene synthesis of derivatives of 1-acetylenyl- and 1-vinyl-3:4-dihydronaphthalene. (FRLN.) E. DANE, O. HÖSS, A. W. BINDSEIL, and J. SCHMITT (Annalen, 1937, 532, 39—51).—Diene syntheses are recorded for 6-methoxy-1-acetylenyl- (I) and -1-vinyl-3:4-dihydronaphthalene (II). 1-Keto-6-methoxy-1:2:3:4-tetrahydronaphthalene does not react with C₂H₂ in the presence of NaNH₂, but with a large excess of MgBr·C₂H₃ gives a little 1-hydroxy-6-methoxy-1-acetylenyl-1:2:3:4-tetrahydronaphthalene (not obtained pure) with (I), b.p. 124—130°/0.5 mm. (formed by dehydration of the alcohol), and di-1-6-methoxy-3:4-dihydronaphthylacetylene, m.p. 177° (formed as main product if less MgBr·C₂H₃ is



used). Maleic anhydride (III) and (I) in Et_2O give 7-methoxy-1:2:9:10-tetrahydrophenanthrene-1:2-dicarboxylic anhydride (IV), m.p. 200°, and 7-methoxy-3:11-endo- α - β -dicarboxyethylene-1:2:3:9:10:11-hexahydrophenanthrene-1:2-dicarboxylic anhydride, m.p. 263° (decomp.), obtained also from (IV) and (III), dissociating into (IV) and (III) at 228–230°/12 mm., resisting hydrogenation, and giving with CH_2N_2 the Me_4 ester, m.p. 195°, of the corresponding tetra-carboxylic acid. Hydrolysis of (IV) by NaOH gives the corresponding dicarboxylic acid, m.p. 206° (decomp.) (Me_2 ester, m.p. 117°); hydrogenation (Pd- CaCO_3) of (IV) in PhOMe gives the H_8 -anhydride, m.p. 181°, converted into the H_8 -dicarboxylic acid, m.p. 185° (decomp.) [Me_2 ester (V), m.p. 123°], which with HBr-AcOH gives 7-hydroxyoctahydrophenanthrene-1:2-dicarboxylic acid, $+0.5\text{H}_2\text{O}$, m.p. 199–200° (decomp.). Partial hydrogenation (Pd- CaCO_3) of (I) gives (II), which with (III) gives 7-methoxyhexahydrophenanthrene-1:2-dicarboxylic anhydride, m.p. 200°, converted by CH_2N_2 into the Me_2 ester, m.p. 117°, of the corresponding acid, which affords (V) when hydrogenated. *p*-Benzoquinone and (I) give oils, but (II) gives 3:6-diketo-10-methoxytetrahydrochrysene, m.p. 150–160° (decomp.). 1-Keto-1:2:3:4-tetrahydronaphthalene and $\text{MgBr}\cdot\text{C}\cdot\text{CH}$ give impure 1-hydroxy-1-acetylenyl-1:2:3:4-tetrahydronaphthalene and di-1:3:4-dihydronaphthylacetylene, m.p. 124°, hydrogenated to α -di-1:1:2:3:4-tetrahydronaphthylethane, m.p. 77°; heating the alcohol with porcelain at 100° gives 1-acetylenyl-3:4-dihydronaphthalene, b.p. 112°/2 mm., which does not react with (III). Partial hydrogenation gives 1-vinyl-3:4-dihydronaphthalene, which with (III) gives hexahydrophenanthrene-1:2-dicarboxylic anhydride, m.p. 213° [hydrolysed to the dicarboxylic acid, m.p. 214–215° (decomp.) (Me_2 ester, m.p. 99°)], and with *p*-benzoquinone gives 3:6-diketotetrahydrochrysene, m.p. 145–146°. R. S. C.

Molecular resonance systems. V. New phthaleins. G. SCHWARZENBACH and M. BRANDENBERGER (Helv. Chim. Acta, 1937, 20, 1253–1260).—Reduction of nitrated diphenylphthalide gives a non-separable mixture of products from which phenolphthalein (I) is obtained in small quantity through the tetrazonium salt. $\text{C}_6\text{H}_4\langle\text{CCl}_2\text{CO}\rangle\text{O}$ condenses satisfactorily with NPhMe_2 (Friedel-Crafts) but the method is useless with NH_2Ph and unsatisfactory with NHPhAc . $\text{CO}(\text{NHPh})_2$ with $\text{o-C}_6\text{H}_4\langle\text{CCl}_2\text{CO}\rangle\text{O}$ and AlCl_3 in PhNO_2 gives an amorphous product (II) converted by conc. HCl at 140° into CO_2 and 4:4'-diaminodiphenylphthalide (anilinephthalein) (III), m.p. 204°, the colourless solution of which in cold AcOH becomes violet when warmed whilst it is colourless in neutral or basic media or in strong acids. 4:4'-Diaminodiphenylphthalimide is obtained from (II) and conc. NH_3 at 130°. The constitution of (III) is established by its conversion into (I), only a small proportion of which can be caused to crystallise, so that the remainder is identified by conversion through the oxime, m.p. 212°, into *p*-hydroxybenzoyl-*o*-benzoic acid, m.p. 213°. Ditolylphthalide is oxidised

by CrO_3 in AcOH to diphenylphthalide-4:4'-dicarboxylic acid, m.p. 304°, transformed by successive treatments with boiling SOCl_2 and NH_3 in CCl_4 into the corresponding diamide, m.p. 313°, which is degraded (Hofmann) to (III). (III) with boiling Ac_2O gives non-cryst. acetanilidephthalein of indefinite m.p. 4:4'-Dibenzenesulphonamidophenylphthalide is amorphous. Dithiophenolphthalein is described.

H. W.

3':5':3'':5''-Tetrabromo-4':4''-dihydroxy-1:4-diphenylnaphthalene-2:3-dicarboxylic anhydride. R. WEISS (Monatsh., 1937, 71, 6–9).—2:5-Di-(*mm'*-dibromo-*p*-hydroxyphenyl)-3:4-benzofuran (I) with maleic anhydride in PhMe yields a cryst. additive product, which with HCl-EtOH affords 3':5':3'':5''-tetrabromo-4':4''-dihydroxy-1:4-diphenylnaphthalene-2:3-dicarboxylic anhydride, m.p. 353°. The Et_2 ester, m.p. 195–196°, is similarly formed from (I) and $(\text{CH}_3\text{CO}_2\text{Et})_2$. J. D. R.

Substance, $\text{C}_{15}\text{H}_{16}\text{O}_7$, m.p. 154–156°, from urine.—See A., III, 384.

Reaction of maleic anhydride with α - and β -benzaldoxime: benzoylaspartic acid. G. LA PAROLA (Gazzetta, 1937, 67, 481–486).—Either α - or β -benzaldoxime with maleic anhydride in C_6H_6 gives benzoylaspartic acid and PhCHO. E. W. W.

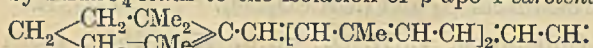
Synthesis of *o*-cyano-aldehydes. I. S. N. CHAKRAVARTI and K. GANAPATI (J. Indian Chem. Soc., 1937, 14, 463–467).—*o*-Cyanobenzaldehyde (I), m.p. 76°, is obtained (in poor yield) by KMnO_4 - Na_2CO_3 oxidation of *o*-cyanocinnamic acid (A., 1928, 835); $\text{o-CN}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and an acid, m.p. 197–202°, are also formed. Similarly 6-cyano-3-methoxybenzaldehyde, m.p. 107°, is obtained, with a substance, m.p. 218°, and an acid, m.p. 132°, by oxidation of 6-cyano-3-methoxy-, m.p. 220°, obtained from 6-amino-3-methoxy-cinnamic acid, m.p. 186° [hydrochloride, m.p. 204° (decomp.)] (from the NO_2 -acid). 2-Amino-3-methoxy-, m.p. 189° (decomp.), is converted into 2-cyano-3-methoxy-cinnamic acid, m.p. 149°. Attempts to convert *o*- NH_2 -derivatives of Schiff's bases, oximes, and acetals into cyano-aldehydes through the diazo-compounds were not successful. E. W. W.

(A) Preparation of some *p*-dialkylaminobenzaldehydes. (B) Condensations of *p*-dialkylaminobenzaldehydes with nitrotoluenes. J. F. J. DIPPY, L. T. HOGARTH, H. B. WATSON, and F. R. WILLIAMS (J.S.C.I., 1937, 56, 346–348r, 396–397r).—(A) Different methods of preparing the aldehydes are compared, with special reference to the yields of *p*- β -hydroxyethylalkylaminobenzaldehydes which can be obtained. The following new aldehydes are described; *p*-ethyl- β -hydroxyethylamino-, m.p. 45–47° [semicarbazone, m.p. 194° (decomp.)], *p*- β -hydroxyethylbutylamino- (semicarbazone, m.p. 158–160°), and 2-methyl-4- β -hydroxyethylbutylamino-benzaldehyde, b.p. 183°/5 mm. (semicarbazone, m.p. 151°). They are best prepared from the appropriate *tert.* bases by a modification of the method of Walter (G.P. 118,567).

(B) The following new stilbenes have been obtained by the interaction of 2:4-dinitrotoluene with the required aldehydes in presence of a little piperidine:

2 : 4-dinitro-4'-diethylamino-, m.p. 149°, 2 : 4-dinitro-4'-ethyl-β-hydroxyethylamino-, m.p. 174—176°, 2 : 4-dinitro-4'-β-hydroxyethylbutylamino-, m.p. 220°, and 2 : 4-dinitro-4'-β-hydroxyethylbutylamino-2'-methylstilbene, m.p. 120°. 2-Nitro-4-amino-4'-dimethylaminostilbene is obtained by reduction of 2 : 4-dinitro-4'-dimethylaminostilbene by ammonium sulphide. It is difficult or impossible to condense aldehydes with *p*-nitrotoluene. 4-Nitro-4'-dimethylaminostilbene is obtained in 46% yield from *p*-dimethylaminobenzaldehyde and *p*-nitrophenylacetic acid in presence of piperidine.

β-apo-4-Carotenal, a further degradation product of β-carotene. P. KARRER, U. SOLNSEN, and W. GUGELMANN (Helv. Chim. Acta, 1937, 20, 1020—1024; cf. A., 1937, II, 378).—Further examination of the products of the oxidation of carotene by KMnO₄ leads to the isolation of β-apo-4-carotenal,



CMe:CHO [oxime, m.p. 165°; semicarbazone, m.p. 217° (decomp.) after softening at 214°], and ψ-α-carotene, m.p. 169—170°. It is proposed to base the names of the compounds obtained by the stepwise oxidation of carotenoids on that of the carotenoid and to indicate the shortening of the chain by the prefix "apo"; the number indicates the distance of the affected from the terminal double linking. Hence carotenal (*loc. cit.*) is β-apo-2-carotenal.

H. W.

Preparation of cyclobutanone. N. J. DEMIANOV and S. M. TELNOV (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 529—538).—1-cyclobutanespirohydantoin and 8% aq. NaOH (14 hr. at the b.p.) yield 1-aminocyclobutane-1-carboxylic acid, m.p. 245—248° (decomp.), converted by the action of HNO₂ into 1-hydroxycyclobutane-1-carboxylic acid (I), and by aq. NaOCl into the chloroamine, which yields cyclobutanone (II) in 74% yield when steam-distilled. (I) does not give (II) when heated with H₂SO₄. R. T.

Catalytic hydrogenation of cyclohexanone. B. FORESTI (Annali Chim. Appl., 1937, 27, 359—365).—Hydrogenation (Pt) of cyclohexanone produces cyclohexanol (I) with a little cyclohexane (II) when carried out in acid medium (H₂SO₄-N-K₂SO₄, *p_H* 1) but only (I) in alkaline medium (*p_H* 12). (II) is produced directly from (I) in acid medium. A nomogram has been constructed by means of which the proportions of the substituents in the ternary mixture may be calc. from the amount of H₂ consumed and the *n* of the org. phase.

L. A. O'N.

Action of primary amines on αβ-dibromopropiophenone. B. REICHERT and F. MOLDENHAUER (Arch. Pharm., 1937, 275, 537—540).—COPh·CHBr·CH₂Br and NH₂Me in C₆H₆ give β-bromo-α-methylaminopropiophenone, m.p. <0° [hydrobromide, m.p. 177—178° (decomp.)], Ph α-methylaminovinyl ketone, m.p. 170—172° (decomp.) [hydrobromide, m.p. 261—263° (decomp.)], and di-[β-bromo-α-benzoyl ethyl]methylamine, m.p. 222—223° (decomp.). NH₂Et gives similarly β-bromo-α-ethylaminopropiophenone hydrobromide, m.p. 172—173° (decomp.).

R. S. C.

Action of hydrogen bromide on benzaldehyde and methyl ethyl ketone. (SIGNA.) G. MASSARA (Gazzetta, 1937, 67, 440—443; cf. A., 1933, 716).—PhCHO + COMeEt with dry HBr give benzylidenobutanone, the compound C₁₈H₁₇OBr (A., 1916, i, 372), and 3 : 4-diphenyl-2-benzylidene-5-methyl-Δ³-cyclopentenone, new m.p. 160—161° (cf. A., 1929, 703).

E. W. W.

Substances containing the β-ionone ring.
Action of organomagnesium compounds on β-ionone. A. GIACALONE (Gazzetta, 1937, 67, 464—468).—β-Ionone (I), CH₂Br·CO₂Et, and Mg give a better yield of Et δ-(1 : 1 : 3-trimethyl-2-Δ²-cyclohexenyl)-β-methylbutadiene-α-carboxylate than when Zn is used (A., 1932, 852), but ionene (II) is also formed. From (I) and MgMeI, (II) and CH₄ are obtained; using MgBu^δBr, a small amount of (II) is formed.

E. W. W.

Oxidation of desylamine and benzoin methyl ether.—See A., I, 623.

Phenyl benzyl ketimine and derivatives. K. N. CAMPBELL (J. Amer. Chem. Soc., 1937, 59, 2058—2061).—Ph benzyl ketimine (I), m.p. 57°, obtained from its hydrochloride (II), m.p. 210—211° (decomp.) [prep. from PhCN and CH₂Ph·MgCl (excess) followed by HCl], hydrolyses rapidly in moist air to NH₃ and COPh·CH₂Ph. The N-Cl-derivative (III), m.p. 78°, of (I) is obtained from (I) (in CHCl₃) and aq. NaOCl; (III) and HCl in light petroleum give (II). (III) does not lose HCl (to give a cyclic imine) when treated with Ag₂O (in C₆H₆) or dry KOH (in Et₂O); with aq. EtOH-KOH, benzoic acid and gummy products are produced. The N-Br-derivative, m.p. about 55°, of (I) is prepared from (II) and aq. KOBr.

H. B.

Reduction of unsaturated ketones. J. F. J. DIPPY and R. N. LEWIS (Rec. trav. chim., 1937, 56, 1000—1006).—Reduction of substituted Ph styryl ketones to the corresponding saturated ketones is best effected by Na and AcOH; secondary diketonic products are formed only at elevated temp. Cl or NO₂ inhibits reduction. The following new or revised data are recorded: Ph *o*-methoxystyryl ketone, m.p. 57°; Ph *o*-chlorostyryl ketone, m.p. 48°; Ph *p*-chlorostyryl ketone, m.p. 114.5°; Ph *o*-nitrostyryl ketone, m.p. 126°; benzylacetophenone-2 : 4-dinitrophenylhydrazone, m.p. 166° (the corresponding semicarbazone could not be obtained); αγδζ-tetra-phenylhexane-αζ-dione, m.p. 243°; Me δ-phenyl-*n*-butyl ketone, b.p. 160—162°/20—23 mm. (semicarbazone, m.p. 156—157°); Ph β-*o*-methoxyphenylethyl ketone, b.p. 227—230°/20 mm. (2 : 4-dinitrophenylhydrazone, m.p. 104.5°); αζ-diphenyl-γδ-dianisylhexane-αζ-dione, m.p. 232°. Styryl Me ketone is reduced (Clemmensen) to *n*-propylbenzene. H. W.

o-Nitrochalkones. I. TANASESCU and A. BACIU (Bull. Soc. chim., 1937, [v], 4, 1742—1759).—Interaction of *o*-NO₂·C₆H₄·CHO with the appropriate substituted acetophenone in EtOH affords the following: 2-nitro-, m.p. 124°, 4'-chloro-2-nitro-, m.p. 148°, 4'-bromo-2-nitro-, m.p. 137°, 2-nitro-4'-methyl-, m.p. 111°, 2-nitro-3' : 4'-dimethyl-, m.p. 128°, 2-nitro-2' : 4'-dimethyl-, m.p. 93°, 2-nitro-2' : 5'-dimethyl-, m.p. 102°, 2 : 2'-dinitro-, m.p. 152—153°, 2 : 4'-di-

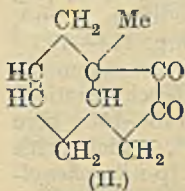
nitro-, m.p. 179°, 2-nitro-4'-cyano-, m.p. 186—187°, 2-nitro-4'-carboxy-, m.p. 245—246° (*Me* ester, m.p. 173—174°), 6'-chloro-2-nitro-3'-methyl-, m.p. 117°, 2:3'-dinitro-4'-methyl-, m.p. 195°, 4'-bromo-2:3'-dinitro-, m.p. 202—203°, 2-nitro-4'-amino-, m.p. 178—181°, and forms, m.p. 82° and 184° (hydrochloride, m.p. 207—210°; semicarbazone, m.p. 203—204°; *Ac* derivative, m.p. 234° and 230—231°), 2-nitro-4'-benzamido-, m.p. 182—183°, 2-nitro-4'-dimethylamino-, m.p. 110—111°, 2-nitro-4'-methylamino-, m.p. 153—154°, 2-nitro-3'-acetamido-, m.p. 182° (phenylhydrazones, m.p. 98°), 2-nitro-3'-amino-, m.p. 142° (hydrochloride, m.p. 195—199° decomp.), 2:3'-dinitro-4'-amino-, m.p. 240—241°, and 3':5'-dibromo-2-nitro-4'-amino-chalkone, m.p. 208—209°. 1:4- $C_{10}H_6Me \cdot COMe$ and $o\text{-NO}_2 \cdot C_6H_4 \cdot CHO$ yield 4-methyl- α -naphthyl 2-nitrostyryl ketone, m.p. 111—112°. When boiled with $EtOH \cdot NaOH$, these chalkones yield red solutions which with conc. HCl afford indigotin. They are decomposed by sunlight. Those chalkones having electropositive substituents are liable to exhibit polymorphism. J. D. R.

Retene. IX. Synthesis of 5:6-benzoretene and its derivatives. D. E. ADELSON and M. T. BOGERT (J. Amer. Chem. Soc., 1937, 59, 1776—1782).—6-Acetylretene and Br in cold Et_2O give 6-bromoacetyl- (I), m.p. 98.5—99°, and a little 6-dibromoacetyl-retene, m.p. 157.5—158°; both are oxidised (I—KI in dioxan—10% $NaOH$) to retene-6-carboxylic acid (II). (I) and $CHNa(CO_2Et)_2$ in C_6H_6 lead to β -6-retoylpropionic [γ -keto- γ -1-methyl-7-isopropyl-6-phenanthrylbutyric] acid (III), m.p. 201—202° [*Me* ester, m.p. 108—109° (oxime, m.p. 126—127°)], also prepared from retene, $(CH_2 \cdot CO)_2O$, and $AlCl_3$ in C_6H_6 , which is reduced (Clemmensen) to γ -6-retylbutyric acid (IV), m.p. 179—179.5° [*Me* ester (V), m.p. 66.5—67.5°]. (III) is oxidised ($NaOCl$) to (II). (IV) and $SnCl_4$ at 105—110°, or its chloride and $AlCl_3$ in C_6H_6 , give 1'-keto-1':2':3':4'-tetrahydro-5:6-benzoretene (VI), m.p. 139.5—140° [oxime, m.p. 203—204° (decomp.); semicarbazone, m.p. 242—244° (decomp.)], reduced (Wolff) to 1':2':3':4'-tetrahydro-5:6-benzoretene, m.p. 88—89° (picrate, m.p. 159—160°), which is dehydrogenated (S at 220—230°) to 5:6-benzoretene, m.p. 98—99° (picrate, m.p. 144—144.5°). (VI) is reduced (Na , $EtOH$) to the 1'-OH-derivative, m.p. 131—132° (picrate, m.p. 154.5—155°). The product from (V), $Et_2C_2O_4$, and $NaOEt$ is converted by 80% H_2SO_4 at 100° into 3':4'-dihydro-5:6-benzoretene-1':2'-dicarboxylic anhydride, m.p. 219—220° (corresponding *Me* ester, m.p. 145.5—146.5°), dehydrogenated (S at 230—250°) to the anhydride (VII), m.p. 244.5—245.5°, of 5:6-benzoretene-1':2'-dicarboxylic acid, m.p. 240—241° (decomp.). (VII) appears to have no cestrogenic activity. β -6-Retoyl- α -methylpropionic acid, m.p. 210—211° [*Me* ester, m.p. 96—97° (oxime, m.p. 135—135.5°)], prepared (as above) from (I) and $CNaMe(CO_2Et)_2$ or from retene and methylsuccinic anhydride, is reduced (Clemmensen) to γ -6-retyl- α -methylbutyric acid, m.p. 131—132°, which is converted (85% H_2SO_4) into 1'-keto-2'-methyl-1':2':3':4'-tetrahydro-5:6-benzoretene, m.p. 120.5—121.5°. All m.p. are corr. H. B.

Additive products of o-nitrobenzaldehyde with substituted acetophenones. I. TANASESCU and A. BACIU (Bull. Soc. chim., 1937, [v], 4, 1673—1683; cf. A., 1932, 625).— $o\text{-NO}_2 \cdot C_6H_4 \cdot CHO$, $COMeR$ ($R = Ph$ etc.), and Na_3PO_4 in aq. $EtOH$ yield the following OH-ketones (m.p. of respective *Bz* derivatives given within parentheses): phenyl (improved yield), p-chloro-, m.p. 97° (179°), and p-bromo-phenyl, m.p. 116° (174°), p-tolyl, m.p. 82° (170°), 4-o-xylyl, m.p. 98—99° (158—159°), p-anisyl, m.p. 139.5° (143°) (also obtained using $KOH \cdot EtOH$), o-, m.p. 139°, and p-nitrophenyl, m.p. 127° (155°), p-cyano-, m.p. 138.5—139° (147—148°), and 4-bromo-3-nitro-phenyl, m.p. 152° (205—207°), 2-nitro-p-tolyl, m.p. 131°, and p-carboxyphenyl β -hydroxy- β -o'-nitrophenylethyl ketone, m.p. 219—220° (226—227°). All the above compounds, especially the last, readily yield indigotin when treated with alkali. m- and p-Amino-, 3-nitro-4-amino-, 3:5-dibromo-4-amino-, 2:5- and 2:4-dimethyl-, and 2-chloro-5-methyl-acetophenone yield only compounds of type $CHR \cdot CH \cdot COR'$. E. W. W.

Syntheses in the hydroaromatic series. I. Condensation of methylcyclopentenone with butadiene. (FRLN.) E. DANE, J. SCHMITT, and C. RAUTENSTRAUCH (Annalen, 1937, 532, 29—38).— $\cdot CO \cdot CO \cdot$ activates an $\alpha\beta$ -ethylenic linking, at least in the cyclopentane ring, to make it reactive towards $(CH_2 \cdot CH)_2$. cyclopentene and SeO_2 in Ac_2O give Δ^2 -cyclopentenyl acetate, b.p. 154—155°, and Δ^4 -cyclopentene-1:3-diol diacetate, b.p. 120—130°/15 mm.; the former is the main product at 100° in an open vessel and the latter in a closed tube at 100°. The monoacetate with cold 2N- $NaOH$ gives Δ^2 -cyclopentenol, b.p. 137° (phenylurethane, m.p. 128—129°; dinitrobenzoate, m.p. 126°). The diacetate is hydrolysed by H_2O and with aq. $NaHCO_3$ rapidly gives Δ^4 -cyclopentene-1:3-diol, b.p. 107°/12 mm., which reduces warm Fehling's solution and ammoniacal $AgNO_3$ or Ag_2CO_3 (slowly in the cold), and gives no cryst. phenylurethane or dinitrobenzoate; use of dil. alkali hydroxide leads to an isomeric diol, which gives a diphenylurethane, m.p. 195°, and diurethane, m.p. 123°. Δ^1 -Methylcyclopentene and SeO_2 give a 35% yield of 2-methyl- Δ^2 -cyclopentenyl acetate (I), b.p. 60—60.5°/12 mm., with some diacetate and methylcyclopentenone; cold KOH or $NaOH$ hydrolyses (I) to 2-methyl- Δ^2 -cyclopentenol, m.p. 59.5—60°/12 mm. (phenylurethane, m.p. 103°), but use of crude (I) leads also to some 5:2'-methyl- Δ^2 -cyclopentenyl-2-methyl- Δ^2 -cyclopentenone, b.p. 115°/0.1 mm., m.p. 106°. Oxidation (CrO_3) leads to 2-methyl- Δ^2 -cyclopentenone, b.p. 53°/12 mm. [semicarbazone, m.p. 213° (slow heating), 220° (decomp.; rapid heating); oxime, m.p. 128°], which with SeO_2 in $AcOH$ at 120° gives Δ^3 -cyclopentene-1:2-dione, m.p. 85° (oily enolic form; quinoxaline, m.p. 135°). This adds $(CH_2 \cdot CH)_2$ in dioxan at 110—130° to give the diketone (II), m.p. 110°.

R. S. C.
Condensation of fluorene with acetone. II. H. FRANCE, P. MAITLAND, and S. H. TUCKER (J.C.S., 1937, 1739—1745; cf. A., 1930, 85).—Fluorene (I) with



COMe₂ containing KOH gives a 50% yield of *Me* β-9-fluorenylisobutyl ketone (II), m.p. 77—78° (piperonylidene, m.p. 167—168°, and 6-bromopiperonylidene derivative), also obtained less well using mesityl oxide (III), (I), and KOH or from (III) and Na fluorenyl (IV) in Et₂O. Fluorenol, obtained from fluorenone (V) by Mg in MeOH at 45°, gives 9-bromo- and thence by AgNO₃ in hot MeOH 9-methoxyfluorene, which gives (IV) by Schlenk's method. With CH₂Ph·OBz (IV) gives 9-benzoylfluorene. Neither 9-fluorenyldimethylcarbinyl chloride nor bromide reacts with CHAcNa·CO₂Et. Dry distillation of (II) gives (I), (III), and COMe₂; heating with KOH·EtOH, Na in xylene, or K in C₆H₆ gives (I); K gives also 9-isopropylidenefluorenone, which, when kept, yields (V). Oxidation of (II) with KMnO₄ gives (?) β-hydroxy-β-9-fluorenylisobutyl *Me* ketone, m.p. 120—122°; with Na₂Cr₂O₇ gives (V), with NaOBr, CHBr₃, and with NaOI, CHI₃. The semicarbazone, m.p. 218°, of (II) with NaOEt gives β-9-fluorenyl-β-methylpentane (VI), m.p. 84—85°, also obtained by Clemmensen reduction, with a substance (VII), C₁₉H₂₀, m.p. 103—104° (formed as sole product by HI). CMe₂Pr⁺Cl (modified prep.) gives a Grignard reagent, which with (V) affords (VI), which is also obtained from the chloride and Et sodiofluorene-oxalate (VIII) or, in very poor yield, potassiofluorene-carboxylate. α-9-Fluorenylisopropyl iodide, m.p. 95—97°, is prepared from the alcohol. Bu⁺I or Bu⁺Cl with (VIII) gives 2% of *tert.*-butylfluorene, m.p. 101—102°. With HBr·AcOH (II) gives a substance, m.p. 95—105°, which rapidly decomposes to HBr and a substance, C₁₉H₁₈, m.p. 77—79°, oxidised to a *keto-acid*, C₁₉H₁₈O₃, m.p. 163—164°, and hydrogenated (Pd) in warm AcOH to (VII). With ZnCl₂ at 240—250° (II) gives (VII) and a substance, C₁₆H₁₄, m.p. 133—134°, also obtained by P₂O₅ at 250°. The *oxime*, m.p. 109—110° (*Ac* derivative, m.p. 90—94°), of (II) with PCl₅ gives an *amide*, C₁₉H₂₁ON, m.p. 167—169°, yielding uncrystallisable bases when hydrolysed. The *Br-*, m.p. 83—85°, *Br₂-*, anhyd. and +EtOH, m.p. 102—104°, and *Br₃-*, m.p. 173—175°, -derivatives of (II) are oxidised (CrO₃) to (V) and thus do not contain Br in the nucleus; no acid was obtained from the *Br₃*-compound by KOH. With HNO₃·H₂SO₄·AcOH (II) gives a *NO₂*-derivative, m.p. 110—114° (in one experiment a substance, C₁₆H₁₅O₃N, m.p. 98—100°), reduced by Na₂S to a substance, C₁₉H₂₁ON, m.p. 143—146°. R. S. C.

Hydroxybenzofluorenones.—See B., 1937, 1025.

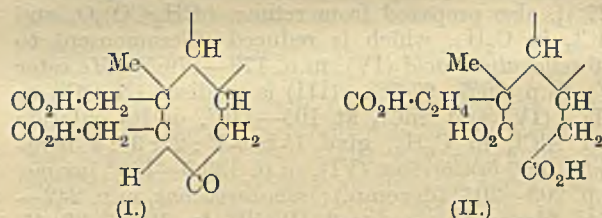
Preparation of 2-hydroxy-5-methoxyacetophenone. F. MAUTHNER (J. pr. Chem., 1937, [ii], 149, 324—327).—*p*-C₆H₄(OAc)₂ (modified prep.), m.p. 121°, and *p*-OMe·C₆H₄·OAc (I), b.p. 134—135°/18 mm., do not undergo the Fries rearrangement. MeCN and (I) do not undergo the Hoesch reaction. *p*-C₆H₄(OH)₂, AcOH, and ZnCl₂ at 145—150° give 2:5-dihydroxyacetophenone, m.p. 202°, which with NaOH·Me₂SO₄ gives the 5-Me ether (*p*-nitrophenylhydrazone, m.p. 215—216°). R. S. C.

Dioximes. CXXIII. G. PONZIO and G. TAPPI (Gazzetta, 1937, 67, 518—526).—Phenylmethyltriketone-“α”-trioxime (I) (A., 1936, 1383) and N₂O₄

give α-phenyl-γ-methyltriketone-trioxime α- and β-peroxides, and the αβ-peroxide, i.e., the *oxime*, OH·N:CMe·C—CPh (II), m.p. 135° (*Ac* derivative, N·O·O·N

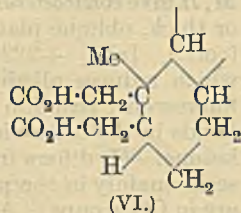
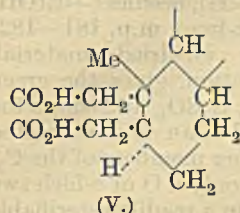
m.p. 100°; *Bz* derivative, m.p. 130—131°), of acetylphenylglyoxime [α-phenyl-γ-methyltriketone-αβ-dioxime] peroxide, m.p. 79—80° [phenylhydrazone, m.p. 160°; semicarbazone, m.p. 218—219° (decomp.)], obtained by HCl hydrolysis of (II), into which it is reconverted by NH₂OH·HCl. With N₂O₄ in Et₂O, or with HNO₃ (*d* 1.40), (II) gives phenyl-(α-dinitroethyl)glyoxime peroxide, m.p. 135—136°. Phenylmethyltriketone-“β”-trioxime (III) (A., 1922, i, 1039) is distinguished from (I) by the m.p. of its *Bz₃* derivative, m.p. 181—182°; with N₂O₄ (III) gives the same products as (I). “β”-Benzoylmethylglyoxime (A., 1922, i, 1038) (semicarbazone, m.p. 247—248°) with Me₂SO₄ yields a Me₂ ether, m.p. 68—69°. E. W. W.

Sulphonic acids of sterol derivatives. A. WINDAUS and E. KUHR (Annalen, 1937, 532, 52—68).—Δ⁴-Cholestenone and Ac₂O·H₂SO₄ give an 85% yield of the 6-sulphonic acid (I), m.p. 193—195° (decomp.) [various salts described; *Me* ester, m.p. 149—150°; phenylhydrazone, m.p. 212—214° (decomp.)]. The alkali salts foam in H₂O, are colloidal, and, as does also (I), cause cholesterol, benzpyrene, and methylcholanthrene to remain dissolved in H₂O. Hydrogenation in the presence of Pd·C in AcOH gives a *H₂-acid*, m.p. 223—225° (decomp.) (*Me* ester, m.p. 172—173°), but use of PtO₂ leads to a *H₁-acid*, sinters at 190°, decomp. 200° (*Me* ester, m.p. 155°), oxidised to the acid (II), C₂₆H₄₄O₅, m.p. 218—220°. The position of the SO₃H is determined by



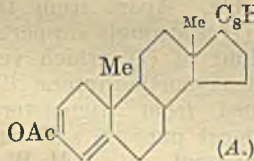
oxidation of (I) by KMnO₄ to the acid (III), C₂₆H₄₄O₆, m.p. (anhyd.) 136—141° and (+AcOH) 97—99°, and cholestane-3:6-dione-4:5-diol, m.p. 220—225° (decomp.) after sintering at 210°, which readily loses H₂O (e.g., with 5% HCl·EtOH) to give the enolic Δ⁴-cholestene-3:6-dion-4-ol, m.p. 148—149°, also obtained from Δ⁴-cholestene-3:6-dione (IV). Sulphonic acids are also prepared from (IV), decomp. about 150° [*Cu* salt; *Me* ester, m.p. 164—165° (decomp.)], Δ⁵-cholesten-7-one, m.p. 178—180° (decomp.) [*Me* ester, m.p. 180—181° (decomp.)], androstenedione, decomp. about 196° [*Me* ester, m.p. 159—160° (decomp.)], and progesterone, m.p. 190—192° (decomp.) (*Me* ester, m.p. 160—161°). Cholestan-3-one gives the 2-sulphonic acid, m.p. about 148° after sintering [*Me* ester, m.p. 206—208° after sintering; phenylhydrazone, m.p. about 180° (decomp.)], oxidised by CrO₃ or HNO₃ to the acid (V), m.p. 191—194° (*Me* ester, new m.p. 60°) (A., 1914, i, 1066), and 2-bromocholestanone gives the enol *acetate*, m.p. 106—107°. Coprostanone gives similarly the 2-sulphonic acid (*Me* ester, m.p. 171—172°, and an isomeric ester), oxidised

to the acid (VI), m.p. 201—202°. *Cholesterylene-x-sulphonic acid* (Me ester, m.p. 175—176°; Li, decomp.



from 220°, Na, and K salts) has little or no antirachitic activity. R. S. C.

Enolic derivatives of progesterone and other $\alpha\beta$ -unsaturated steroid ketones. U. WESTPHAL (Ber., 1937, 70, [B], 2128—2136; cf. A., 1937, II, 25).—Treatment of testosterone (I) with boiling Ac_2O — AcCl gives the enol diacetate, m.p. 153—155°, $[\alpha]_D^{20}$ —151° in CHCl_3 , hydrolysed by H_2SO_4 to (I); it shows protracted physiological activity. Progesterone (II) is transformed into the corresponding enol acetate, m.p. 138°, $[\alpha]_D^{20}$ —41.9° in CHCl_3 , and enol propionate, m.p. 134—136°, $[\alpha]_D^{20}$ —40.6° in CHCl_3 , by a mixture of the requisite acid anhydride and chloride, whereas for the prep. of the enol butyrate, m.p. 116—118°, $[\alpha]_D^{20}$ —37.8° in CHCl_3 , it is necessary to use $\text{Pr}^n\text{CO}_2\text{Na}$ and $(\text{Pr}^n\text{CO})_2\text{O}$. Physiologically the action of these esters is practically indistinguishable from that of (II), to which they are somewhat inferior. The ultra-violet absorption spectra of the esters establishes the presence of a conjugated double linking similar to that of cholestenone enol acetate (III). This does not react readily with maleic anhydride (IV) and under more drastic conditions a product, m.p. about 260° (decomp.), mol. wt. about 1800 (very sparingly sol. Na salt), is produced. It differs from all known adducts of (IV) and sterols. (III) is therefore (A). The double



linkings in the esters are therefore at Δ^3 and Δ^5 .

H. W.

Attempted partial reduction of androstenedione. U. WESTPHAL and H. HELLMANN (Ber., 1937, 70, [B], 2136—2140).—Androstene-3:17-dione is transformed into the 3-monosemicarbazone, decomp. 234°, the constitution of which is established by its absorption spectrum. This is reduced by Na and Pr^nOH and then hydrolysed to testosterone, freed from androstenediol by Girard's "ketone reagent T."

H. W.

Sterols. XX. The pregnanolones. R. E. MARKER, O. KAMM, and E. L. WITTLE (J. Amer. Chem. Soc., 1937, 59, 1841—1843).—Partial reduction (H_2 , PtO_2 , EtOH) of pregnanedione (I) gives *epipregnan-3-ol-20-one*, new m.p. 149° (cf. A., 1937, II, 424) (acetate, m.p. 112°; semicarbazone, m.p. 245°), also obtained by limited acetylation (AcOH — Ac_2O) of pregnanedione and subsequent oxidation (CrO_3). Reduction (H_2 , PtO_2 , AcOH — HBr) of (I) affords mainly *pregnan-3-ol-20-one*, m.p. 149° (acetate, m.p. 121°; semicarbazone, m.p. 245°); androstenedione

similarly gives androsterone. The OH-ketones are purified by treatment of the crude reaction products with Girard's reagent and subsequent prep. of the H succinates. *epialloPregnanolone* has m.p. 176° (cf. *ibid.*, 250). H. B.

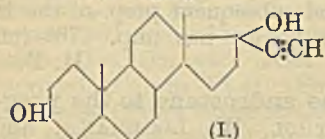
Conversion from the androstane to the pregnane series. J. KATHOL, W. LOGEMANN, and A. SERINI (Naturwiss., 1937, 25, 682).—The conversion is effected by C_2H_2 and its derivatives. Thus dehydroandrosterone and C_2H_2 afford Δ^5 -17-ethynylandrosterone-3:17-diol, m.p. 240° (Ac, m.p. 175°, and Ac_2 derivative, m.p. 169°), which with O_3 yields 3:17-diacetoxyxiocholenic acid, m.p. 246°. *isoAndrosterone* with C_2H_2 gives 17-ethynylisoandrosterone-3:17-diol, m.p. 257°, partly hydrogenated to 17-ethynylisoandrosterone-3:17-diol, m.p. 207°, oxidation of which by perphthalic acid affords the corresponding oxide, m.p. 182°, whilst OsO_4 and reductive degradation gives 3:17:20:21-tetrahydroxyallopregnane. The ethynyl derivatives exhibit more of the characteristics of female than of male hormones. F. O. H.

New compounds of the follicle hormone series. K. MIESCHER and C. SCHOLZ (Helv. Chim. Acta, 1937, 20, 1237—1244).—The enhanced activity of sex hormones induced by suitable esterification is attributed to delayed resorption and consequent better utilisation of the hormone. The delay is due in part to impeded diffusion and probably, in part to solubility and hydrolysis. *Oestrone* (I) and $(\text{CHMe}_2\text{CO})_2\text{O}$ in $\text{C}_5\text{H}_5\text{N}$ at 120—125° yield *oestrone isobutyrate*, m.p. 120—121°; the corresponding *n-hexoate*, m.p. 94.5—95°, and *stearate*, m.p. 81.5—82.5°, are obtained by use of the requisite acid chloride. Similar methods lead to the prep. of *oestradiol* 3:17-diisobutyrate, m.p. 100.5—101.5°, and 3:17-dipalmitate, m.p. 63—65°. *Oestradiol* 3-mono-*n*-butyrate, m.p. 98—99°, and 3-monostearate, m.p. 78—79°, are obtained by hydrogenation (Adams) of the corresponding *oestrone* esters. Partial hydrolysis of the requisite normal esters by K_2CO_3 in 95% MeOH affords *oestradiol* 17-monoisobutyrate, m.p. 183—183.5°, 17-mono-*n*-valerate, m.p. 144—145°, and 17-mono-*n*-hexoate, m.p. 112—112.5°. *Oestradiol* 3-benzoate (from the alcohol and BzCl), *n*-valeric anhydride, and $\text{C}_5\text{H}_5\text{N}$ give *oestradiol* 3-benzoate 17-*n*-valerate, m.p. 133—133.5°. Similar methods lead to *oestradiol* 17-benzoate 3-propionate, m.p. 165—166°, and 17-benzoate 3-*n*-butyrate, m.p. 141.5—142° (hydrolysed to *oestradiol* 17-monobenzoate, m.p. 92.5—94°). Successive treatments of *oestradiol* in dioxan with COCl_2 and MeOH or EtOH afford 17-methylcarbonato-, m.p. 216.5—218°, or ethylcarbonato-, m.p. 171—172°, -*oestradiol*. 3:17-Diethylcarbonato-*oestradiol* has m.p. 138—139°. The Na derivative of (I) and allyl bromide give *oestrone allyl ether*, m.p. 108—109°, which is isomerised in boiling NPhEt_2 to the amorphous *C-allyloestrone* (benzoate, m.p. 155—160°). *Oestrone cinnamyl ether* has m.p. 149—149.5°.

H. W.

Sex hormones. XXIV. Addition of acetylene to the 17-keto-group of *trans*-androsterone and Δ^5 -*trans*-dehydroandrosterone. L. RUZICKA and K. HOFMANN (Helv. Chim. Acta, 1937, 20, 1280—1282).—A solution of K in liquid NH_3 is treated with

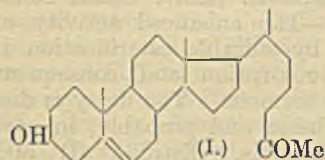
C_2H_2 until it is decolorised and *trans*-dehydroandrosterone in $C_6H_5-Et_2O$ is added; after treatment



with Girard's reagent, the product gives Δ^5 -17-acetylenylandrostene-3-trans-17-diol (I), m.p. 240—242° [3-monoacetate, m.p. 175—176°

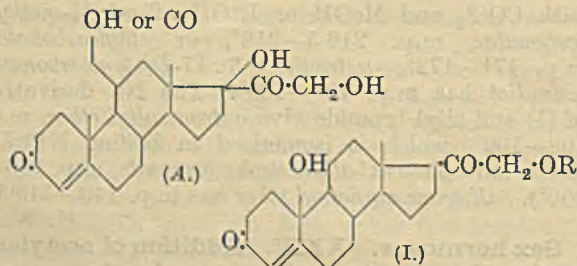
after softening at 170°; diacetate, m.p. 169—169.5°, hydrolysed to (I)]. Similarly *trans*-androsterone gives 17-acetylenylandrostane-3-trans-17-diol, m.p. 255—257° (3-monoacetate, m.p. 205—207°; diacetate, m.p. 199—250°). H. W.

Sex hormones. XXVI. Oxidation of cholesteryl acetate dibromide with chromium trioxide. L. RUZICKA and W. H. FISCHER (Helv. Chim. Acta, 1937, 20, 1291—1297).—The main portion of the acetate of *trans*-dehydroandrosterone is removed as semicarbazone from the debrominated neutral products of the oxidation of cholesteryl acetate dibromide by CrO_3 in AcOH at 28—30°. The mother-liquors give a mixture of semicarbazones which is treated successively with acid and alkali; the product when



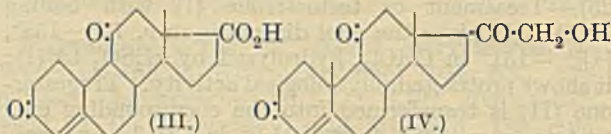
crystallised from MeOH yields Δ^5 -norcholestene-3-trans-ol-25-one (I), m.p. 125—127° [benzoate, m.p. 144—145°; acetate, m.p. 141.5—142°, and its semicarbazone, m.p. 237—238° (decomp.)], oxidised through the dibromide to a diketone, $C_{26}H_{40}O_2$. Catalytic hydrogenation of (I) gives a mixture of the saturated OH-ketone and the corresponding diol, oxidised by CrO_3 to a saturated diketone identical with that derived from epicholestanyl acetate. The constitution of (I) is thus established. (I) is physiologically inactive. The mother-liquors from (I) yield *trans*-dehydroandrosterone and Δ^5 -pregnanolone. H. W.

Constituents of the adrenal gland. X. Corticosterone. T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 953—969; cf. A., 1936, 1382).—Further examination of substance *H* (*loc. cit.*) discloses the presence of substance *M*, an $\alpha\beta$ -unsaturated ketone, $C_{21}H_{30}O_5 \pm H_2$, m.p. 207—210° (corr.; slight decomp.) when slowly heated; it reduces alkaline Ag solution, gives the green fluorescence reaction with conc. H_2SO_4 , the absorption spectrum of an $\alpha\beta$ -unsaturated ketone, and is oxidised by CrO_3 to adrenosterone. It



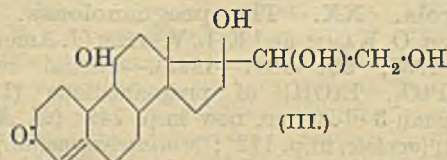
resembles very closely substance *Fa* but is distinguished by cryst. form. It is isomeric with *Fa* or distinguished therefrom by 2H so that the partial

structure *A* is probable for it. It is biologically inactive in the quantity available. After removal of *M*, *H* give corticosterone [(I), R = H], needles (+EtOH) or thick, oblique plates (solvent-free), m.p. 181—182° (corr.), $[\alpha]_D^{25} +223^\circ \pm 3^\circ$ for air-dried material, which reduces alkaline Ag solution, gives the green fluorescence reaction with conc. H_2SO_4 , and shows the bands in the ultra-violet typical of an $\alpha\beta$ -unsaturated ketone. (I) differs from the other members of the C_{21} series mainly in the presence of only 4 O of which two are in CO groups. A third lies in a readily esterifiable OH since (I) gives an acetate (II) [(I), R = Ac], various forms all of m.p. about 145—146.5°, and, after resolidification, m.p. 152.5—153° (corr.), a butyrate, m.p. 170—171° (corr.), very suitable for diagnosis, a benzoate, m.p. 201—202° (corr.), a *H* succinate, m.p. 194—195°, a palmitate, m.p. 87—93°, and an oleate,



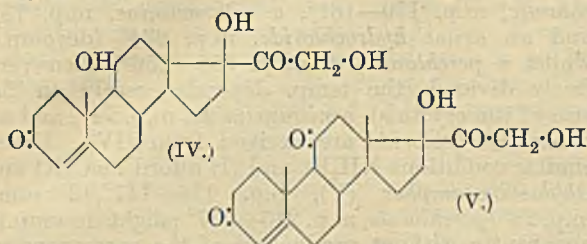
m.p. 79—81°. (I) is oxidised by CrO_3 to the acid (III), m.p. about 266—272° (corr.) [*Me* ester, m.p. 174—178° (corr.)]. The occurrence of the fourth O of (I) in a *sec.* OH is established by the mild oxidation of (II) with CrO_3 to dehydrocorticosterone acetate, m.p. 178—180.5° (corr.), which retains the reducing group; it is hydrolysed to dehydrocorticosterone, m.p. about 177—180° after softening at 170°, identical with the substance *A* of Kendall. The exact position of the *sec.* OH is uncertain but in analogy with substances *A*, *C*, *D*, *E*, *Fa*, and *M* it is probably attached to $C_{(11)}$ or $C_{(12)}$; on purely chemical grounds attachment to $C_{(11)}$ is the more probable. Apart from this uncertainty, the structure of (I) is strongly supported by the physiological behaviour of (I), which very closely resembles that of deoxycorticosterone (21-hydroxyprogesterone) obtained from stigmastrol. Substance *K* (*loc. cit.*) is almost pure (I) and need not be regarded as a new compound. H. W.

Constituents of the adrenal gland. XI. Constitution of the $C_{21}O_5$ group. T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 978—991; cf. A., 1937, II, 380).—The location of the last O of substance *A* (*loc. cit.*) permits further conclusions with regard to the other $C_{21}O_5$ substances since these can all be converted into the same triketone. Substance *E*, anhyd. or (+ H_2O), m.p. about 120° (decomp.), is oxidised by CrO_3 to adrenosterone (I) whereas with HIO_4 it affords Δ^4 -androsten-11-ol-3:17-dione (II), m.p. 189—190° (corr.), readily converted by CrO_3 into



(I). Hence *E* is (III), the position of the double linking being fixed since it has the spectrum of an $\alpha\beta$ -unsaturated ketone and only one CO is now shown to be present. It can therefore be only in Δ^4 or

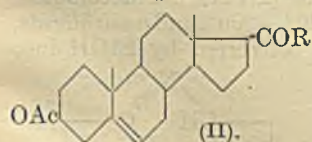
Δ^4 position, the latter being much the more probable by reasons of analogy. Substance *M* is oxidised by CrO_3 in AcOH to (I) and by $\text{Pb}(\text{OAc})_4$ to (II); it



is therefore (IV). Substance *M* gives a *monoacetate*, m.p. 223—225° (corr.), which is not attacked by HIO_4 but is oxidised by CrO_3 in AcOH to the *monoacetate*, m.p. 239—241° after becoming opaque at 70—100°, of substance *Fa* which is therefore (V). Fuller data for substances *C* and *D* could not be obtained owing to lack of material. *C* does not give a pure product with $\text{Pb}(\text{OAc})_4$. *D* gives a *diacetate*, m.p. 224—226° (corr.) after becoming opaque at about 90°, which is oxidised by CrO_3 in AcOH to androstane-3-ol-11:17-dione acetate. *C* yields a *diacetate*, m.p. 204—206°, which gives ill-defined compounds when oxidised. The following identities are established among the compounds isolated by Reichstein (R), Wintersteiner and Pfiffner (W) and Kendall *et al.* (K): substances *A* (R), *A* (W), and *D* (K); *C* (R), *D* (W), and *C* (K); *D* (R) and *G* (K); *Ea* (R), *Fa* (W), and *E* (K); andrenosterone (R) and ketone 4 (K); corticosterone (R) and compound *B* (K); dehydrocorticosterone (R) and compound *A* (K); substance *L* (R) and compound *G* (W); compound *M* (R) and *F* (K). The problem of the isolation of the active hormone is not completely solved since amorphous fractions are isolable from the gland which excel any of the cryst. materials in cortin activity. Either a more powerful substance is present or two components are required for the development of full activity, one of which may be only an activator. The possible mode of biosynthesis is discussed.

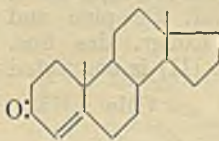
H. W.

Constituents of the adrenal gland. XII. Deoxycorticosterone (21-hydroxyprogesterone) from Δ^5 -3-hydroxy Δ^2 cholonic acid. M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 1164—1179).—Treatment of Δ^5 -3-acetoxy Δ^2 cholonic acid with SOCl_2 in C_6H_6 yields the corresponding *chloride* (I), m.p. about 165° (decomp.) when rapidly heated, frequently accompanied by the *anhydride*, m.p. 331—332° (corr.; slight decomp.). CH_3N_2 and (I) in abs. Et_2O give Δ^5 -21-*diazo*-3-*acetoxy*-*pregnen*-20-one [(II), R = CHN_2], m.p. about 148—150° (decomp.), which does not give a ppt. with digitonin (III) in 80% EtOH , hydrolysed by cold KOH - EtOH to Δ^5 -21-*diazo*-3-*hydroxy*-*pregnen*-20-one (IV), m.p. 144° (corr.; decomp.), which gives an



immediate ppt. with (III) in 80% EtOH . $2\text{N-H}_2\text{SO}_4$ and (II) in dioxan yield Δ^5 -21-*hydroxy*-3-*acetoxy*-*pregnen*-20-one [(II), R = CH_2OH], m.p. 149—156° (corr.), hydrolysed by acid to Δ^5 -21:3-*dihydroxy*-*pregnen*-20-one, m.p. (indef.) 139—159°. Treatment

of (II) in anhyd. Et_2O with HCl at 0° affords Δ^5 -21-*chloro*-3-*acetoxy*-*pregnene*-20-one (V) [(II), R = CH_2Cl], m.p. 157—158° (corr.), whence the corresponding 3-OH-*derivative*, m.p. 162—164°. Both Cl-ketones reduced cold $\text{Ag}_2\text{O-NH}_3$ solution. Direct oxidation of (V) with CrO_3 in AcOH gives mainly Δ^4 -21-*chloro*-*pregnene*-3:6:20-*trione*, m.p. 215—220° (corr.); if the double linking is protected by bromination previous to the oxidation, the reaction occurs in the desired sense but subsequent debromination with Zn or with KI also removes Cl from C_{21} and progesterone results. AcOH converts (IV) into Δ^5 -3-*hydroxy*-21-*acetoxy*-*pregnen*-20-one, m.p. 184—185° (corr.) [the corresponding *Bz* derivative has m.p. 171—173° (corr.)], brominated in CHCl_3 and then oxidised and de-



brominated to Δ^4 -3-*keto*-21-*acetoxy*-*pregnen*-20-one (VI), m.p. 157—159° (corr.), $[\alpha]_D^{25} +177^\circ \pm 4^\circ$ in abs. EtOH , hydrolysed to Δ^4 -3-*keto*-21-*hydroxy*-*pregnen*-20-one (*deoxycorticosterone*), m.p. 141—142° (corr.), $[\alpha]_D^{25} +178^\circ \pm 3^\circ$ in abs. EtOH , the simplest known compound with cortin activity.

H. W.

Oxidation-reduction potentials of hydroxynaphthaquinones in alkaline solutions.—See A. I, 620.

Kinetics of the production of anthraquinone compounds from benzoylbenzoic acid derivatives. R. ODA and K. TAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1937, 32, 263—273).—The rate of cyclisation of *o*- $\text{C}_6\text{H}_4\text{Bz-CO}_2\text{H}$, *o*-4'-toluyl-, *o*-4'-chlorobenzoyl-, *o*- α -naphthoyl-, and *o*-5:6:7:8-tetrahydro-2-naphthoyl-benzoic acid to anthraquinone and its derivatives, under the action of 95.6% H_2SO_4 , is studied at varying temp.; velocity coeffs., and, for the first three reactions, energies of activation, are calc. It is assumed that addition of H_2SO_4 precedes condensation, and that the velocity of addition is significant. *o*-3'-Nitrobenzoylbenzoic acid does not condense. 1-*o*-Carboxyanilinoanthraquinone cyclises very rapidly [to the acridone]. E. W. W.

[Ring] conversion reaction in the reduction of menthones by Clemmensen's method. A. AUTERINEN (Suomen Kem., 1937, 10, B, 22—23).—Menthone *Et* ether with Na dissolving in EtOH affords 3-hydroxy-5-ethoxy-1:1-dimethylcyclohexane, oxidised (CrO_3) to 3-ethoxy-5:5-dimethylcyclohexanone, b.p. 124—126°/32 mm. (*semicarbazone*, m.p. 188—188.5°). 1:1-Dimethylcyclohexane-3:5-diol (A., 1913, i, 607) with Ac_2O in a mixture of boiling EtOAc , CHCl_3 , and C_6H_6 affords the *Ac*₁ (I), b.p. 148—150°/18 mm., and *Ac*₂ derivatives. The former with CrO_3 affords a substance which when distilled in air loses AcOH to give 5-keto-1:1-dimethyl- Δ^2 -tetrahydrobenzene (II), and when distilled in vac. gives 3-*acetoxy*-5:5-dimethylcyclohexanone, b.p. 77—78°/0.044 mm. (I) affords the dinitrophenylhydrazones and semicarbazones of (II). Hydrolysis of (I) with HCl gives (II); with N-NaOH a *dimeride* (?), m.p. 97—99.5°, of (II) is formed. Prolonged action of conc. HCl at room temp. on (II) affords a small amount of an unidentified oil. (II) when reduced (Clemmensen)

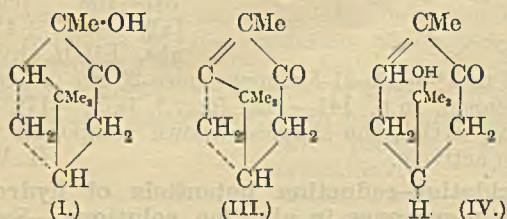
affords a product from which the semicarbazones of 3:3-dimethylcyclohexanone and 2:4:4-trimethylcyclopentanone (cf. A., 1935, 1239) are isolated.

J. L. D.

Electrochemical oxidation of pinene. F. FICHTER and G. SCHETTY (Helv. Chim. Acta, 1937, 20, 1304—1308).—Electro-oxidation at a PbO_2 anode of pinene emulsified by invadin B in aq. H_2SO_4 gives HCO_2H , terebic acid (I), and *p*-cymene. In $\text{EtOH-H}_2\text{SO}_4$ the products are dipentene, cineole, α -terpineol, EtHSO_4 , (I), and *cis*-terpin.

H. W.

New example of the transformation of a given active pinene into two compounds of inverse optical activity (carvones). M. DELÉPINE (Bull. Soc. chim., 1937, [v], 4, 1669—1673; cf. A., 1924, i, 1084, 1088).—The (—)-*keto-alcohol* (I) (cf. Delépine and Grandperrin, Compt. rend. 65e Congr. des Soc. savantes, 1932, 101) from *d*-pinene (II) is converted



into its (+)-semicarbazone, which with $\text{H}_2\text{C}_2\text{O}_4$ in EtOH gives *d*-carvone (yielding *d*-carvoxime). The intermediates (III) and (IV) are suggested. *l*-Carvoxime is obtained from (II) in the usual way through *d*-limonene and its nitrosochloride.

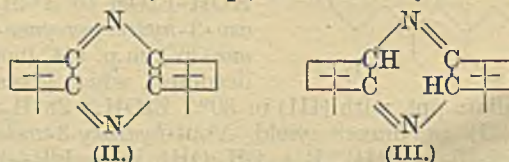
E. W. W.

Thioborneol and isothioborneol. Mercaptides of thioborneol. J. HARASZTI (J. pr. Chem., 1937, [ii], 149, 301—310).—Pure bornyl chloride and MgEtBr give Mg bornyl bromide, which with S gives thioborneol (I), m.p. 112.5—113°, with a little thiocamphor, m.p. 125—130° (oxime, m.p. 118—118.5°), and bornyl disulphide, m.p. 195° [reduced by Zn-HCl to (I)]. *iso*Bornyl chloride (modified prep.), however, gives camphane. Thus (I) is related to borneol; it gives *Pb*, m.p. 250—260° (decomp.), Hg^{II} , m.p. 175°, Cu^{I} , m.p. 120—125°, *Bi*, m.p. 172—175°, and *Au*, m.p. about 195—200° (decomp. 220—230°), salts and *salts*, $(\text{C}_{10}\text{H}_{17}\text{S})_2\text{BiI}$, decomp. 140—150°, and $\text{TiS}\cdot\text{C}_{10}\text{H}_{17}\cdot\text{C}_{10}\text{H}_{17}\cdot\text{SH}$, m.p. 166°. R. S. C.

Action of primary aliphatic bases on camphorquinone. II. H. RUPE and A. T. DI VIGNANO (Helv. Chim. Acta, 1937, 20, 1078—1097; cf. A., 1934, 1224).—Camphorquinone (I) condenses very readily at the β -CO with primary aliphatic amines and under pressure and at $>100^\circ$ the main products are alkylaminocamphors (II) with small amounts of the corresponding epicamphor bases, the alkyl of the amine behaving as reducing agent; pyrazine compounds are also formed. At lower temp. and in open vessels alkylimino-bases of camphor are almost exclusively formed; these are readily hydrogenated to (II). Oxidation of camphor by SeO_2 in boiling Ac_2O gives (I) in 90% yield. (I) and NH_2Me in abs. EtOH at 112—115°/6—7 atm. give $\text{CH}_2(\text{OEt})_2$, isodicamphenepyrazine, methylaminocamphor (III), b.p. 109.5—110°/12 mm., which can be preserved only

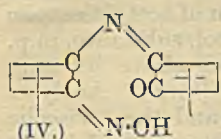
under N_2 in the dark, and methylaminocamphor (IV), b.p. 111.5—112°/11.5 mm., which resinifies less readily than (III) on exposure to air. (III) gives a *perchlorate*, m.p. 179—181°, a *nitrosoamine*, m.p. 73°, and an *oxime hydrochloride*, m.p. 234° (decomp.), whilst a *perchlorate*, decomp. 255—256° when very finely divided (the temp. depends greatly on the size of the crystals), a *nitrosoamine*, m.p. 71°, and an *oxime hydrochloride* are derived from (IV). Under similar conditions NH_2Et and (I) afford MeCHO and ethylaminocamphor (V), b.p. 116—117°/12 mm., m.p. 28° [*perchlorate*, m.p. 215—217° (slight decomp.)], apparently without production of the corresponding *epi*-compound. Me_2SO_4 and (V) readily give methyl-ethylaminocamphor, b.p. 119—119.5°/12.5 mm. [*perchlorate*, m.p. 204—205° (decomp.)], identical with the product obtained by treating (III) with Et_2SO_4 . Methyl-ethylaminocamphor (*perchlorate*, m.p. 184—187°), has b.p. 122—124°/12.5 mm. Reduction (Ni in $\text{EtOH-H}_2\text{O}$) of (III) gives methylaminoborneol, b.p. 131—134°/12 mm. [*hydrochloride*, m.p. 315° (decomp.)], probably not sterically homogeneous. Reduction of (III) with Na and C_6H_6 affords a methylaminoborneol, m.p. 84—85° (*hydrochloride*, m.p. $>300^\circ$ after becoming discoloured at 250°) which contains 2 active H (Zerevitinov). Hydrogenation (Ni in $\text{H}_2\text{O-EtOH}$ at room temp.) of (IV) gives methylaminocamphor, b.p. 134—135°/12 mm., m.p. 116° after softening at 106° (*hydrochloride*, slow decomp. $<250^\circ$), in 95.5% yield. Treatment of (I) with NH_2Me in boiling abs. EtOH for 20 min. followed by preservation at room temp. for 24 hr. gives methylaminocamphor, b.p. 112—114°/11 mm., m.p. 84—85°, $[\alpha]_D^{20} +173.3^\circ$ in C_6H_6 ; it is readily hydrogenated (Na in EtOH) to (III) with a very small proportion of (IV). Similar treatment of (I) with 33% NH_2Et in abs. EtOH yields ethylaminocamphor, m.p. 63—64°, $[\alpha]_D^{20} +176.3^\circ$ in C_6H_6 . Condensation of (I) with NH_3 occurs less readily than with NH_2Me and leads to α -aminocamphor, b.p. 120—122°/14 mm., which, according to the behaviour of its hydrochloride and oxime, is homogeneous. It gives dihydrodicamphenepyrazine, m.p. 114—115°. H. W.

Constitution and synthesis of isodicamphenepyrazine. H. RUPE and A. T. DI VIGNANO (Helv. Chim. Acta, 1937, 20, 1097—1117).—The basic distillate of high b.p. from the condensation of camphorquinone (I) and NH_2Me at high temp. affords isodicamphenepyrazine (II), m.p. 204.5—205°, $[\alpha]_D^{20} +13.23^\circ$ in C_6H_6 [obtained by Einhorn and Jahn (A., 1903, i, 43) from aminocamphor and its hydrochloride], and isodihydrodicamphenepyrazine (III), b.p. 197—198°/12.5 mm., m.p. 71—72°, $[\alpha]_D^{20} +387.63^\circ$ in C_6H_6 , $+330.2^\circ$ in CHCl_3 . (II) gives a methiodide, decomp. 259°, *picrate*, m.p. 204—206°, and *aurichloride*, m.p. 254—255° (decomp.), converted by EtOH into



the "modified salt," decomp. 249—251°. (III) affords a *perchlorate*, decomp. 246.5°, *picrate*, decomp.

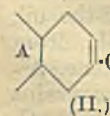
196.5° or 190° when finely divided, *hydriodide*, decomp. 231° after becoming discoloured at 208°, and *methiodide*, decomp. 245–246°, which gives (I) when heated and is transformed by Ag_2O into *N-methylisodihydrodicamphenepyrazinium hydroxide*, m.p. 190–200° after softening at 100° (*picrate*, decomp. 179°).



α - or β -2:3-Diaminocamphane with (I) with ZnCl_2 in AcOH gives (III) in better yield but throws no light on the constitution of the product. Aminocamphoroxime with (I) and cryst. NaOAc in EtOH in the dark at room temp. or, more rapidly, in boiling solution yields *oximinocamphyliminocamphor* (IV), m.p. 174–175° (decomp.) when finely divided, $[\alpha]_D^{20} -225.9^\circ$ in C_6H_6 , which is readily hydrolysed by acids and is hydrogenated (Ni) to (III), also obtained when the mixture of amino-camphor and *-epi*-camphor as obtained by its hydrolysis is preserved for several weeks. Oxidation of (III) readily yields (II) thus establishing the constitution of the latter. Hydrogenation (Ni or Pd at 80°/10 atm.) of (II) or (III) appears impossible but they are converted by Na and EtOH into *isotetrahydrodicamphenepyrazine* (V), m.p. 113.5–114.5°, b.p. 202–204°/11 mm., $[\alpha]_D^{20} +80.60^\circ$ in C_6H_6 [*perchlorate*, decomp. 231–233°; *hydriodide*, m.p. >310°; (NO)₂-derivative, m.p. 144–145° (decomp.)], which contains two active H (Zerevitinov). The following experiments were made in attempts to explain the production of dihydrodicamphenepyrazines by the action of (I) on alkylamines. Methylaminocamphor is unchanged when strongly heated. $\text{NH}_3\text{-EtOH}$ and (I) at 100° give exclusively iminocamphor or, if action is greatly prolonged, a resin-like mass from which a derivative of (III) could not be extracted. MeI in boiling MeOH transforms (V) into *NN'-dimethylisotetrahydrodicamphenepyrazine*, m.p. 86–87°, $[\alpha]_D^{20} +64.88^\circ$ in C_6H_6 (*hydriodide*, decomp. 252–257°; *picrate*, decomp. 151–153°), which reduces acid or neutral KMnO_4 and immediately decolorises Br in CHCl_3 ; it passes at 270–290° into (II), unsaturated hydrocarbons, CO , H_2 , CH_4 , C_2H_6 , and N_2 .

Synthesis of thujane. P. C. GUHA and S. KRISHNAMURTHY (Current Sci., 1937, 6, 56–57).—Et 1-methyl-3-isopropylcyclopentan-2-one-1-carboxylate is reduced (Na-Hg) to the corresponding *sec.* alcohol, b.p. 153–156°/11 mm. (*phenylurethane*, m.p. 144–145°), dehydrated (P_2O_5) to the cyclopentene compound, b.p. 114–115°/11 mm. This substance and CH_2N_2 give the *dicyclo-0:1:3*-hexane derivative, b.p. 130–132°/12 mm., hydrolysed (KOH) to the carboxylic acid, m.p. 93–94°, which is decarboxylated to thujane. F. R. S.

Cedrene. II. Methyl-oxidation of cedrene by selenious acid to primary cedrenol and to cedrenal. W. TREIBS (Ber., 1937, 70, [B], 2060–2066).—Artificial cedrene (I), obtained by short treatment of cedrol with 95% HCO_2H , is oxidised by SeO_2 in Ac_2O to *isocedrenol* (II), b.p. 165°/20 mm., $\alpha_D -76.5^\circ$. (*H phthalate*, m.p. (indef.) 95°; *acetate*, b.p. 174°/20 mm.). Treatment of (II) with hot, 95% HCO_2H gives U (A., II.)



immediately an isomeric, saturated, probably tetracyclic *alcohol*, b.p. 160°/20 mm., $\alpha_D -58^\circ$, oxidised to an *aldehyde* which affords a readily sol. *semicarbazone* and thence to a poorly cryst. monocarboxylic acid. Farther oxidation of (II) by CrO_3 in AcOH-EtOH or more drastic oxidation of (I) with SeO_2 gives *cedrenal*, (III), b.p. 163°/20 mm., $\alpha_D -56^\circ$ [*semicarbazone*, m.p. 248° (decomp.)]. Treatment of (III) with H_2O_2 and KOH-MeOH gives a mixture from which the ester, $\text{C}_{17}\text{H}_{30}\text{O}_4(\text{OMe})_2$, m.p. 111–112°, separates; this is hydrolysed to the acid, $\text{C}_{16}\text{H}_{28}\text{O}_4$, m.p. 158° (decomp.), derived by addition of 1 H_2O and 1 MeOH to cedrenal oxide. Oxidation of (II) with CrO_3 (=20) in AcOH gives *cedrenecarboxylic acid*, m.p. 122° (*Me ester*, m.p. 167–169°/20 mm., $\alpha_D -71^\circ$), isomerised by Br in CHCl_3 to the acid, m.p. 149–150°. Oxidation of (II) with KMnO_4 in aq. COMe_2 yields *norcedrenedicarboxylic acid* (IV), b.p. 330°/atm. pressure, m.p. 209°, which is unusually stable towards chemical reagents. The *Me H* ester, m.p. 97–98° and Me_2 ester, b.p. 173°/20 mm., hydrolysed to an isomeric *Me H* ester, m.p. 124°, are described. H. W.

Terpene compounds. I. Synthetic study on the structure of azulene. N. N. CHATTERJEE (J. Indian Chem. Soc., 1937, 14, 417–420; cf. Bardhan, A., 1935, 748).—Preliminary to attempting the synthesis of azulene, 3-methyl-1-isopropylideneindene (I), m.p. 49°, was synthesised as follows: Et Δ^1 -tetrahydrobenzoate treated successively with Et sodiocyanacetate and $\text{CH}_2\text{Br-CO}_2\text{Et}$ gives *Et 1-carbethoxycyclohexane-2- α -cyanosuccinate*, b.p. 204–206°/4 mm., hydrolysed and esterified to the *Et 1-carbethoxy-2-succinate*, b.p. 177–185°/7 mm. This with Na yields *Et (0:3:4-dicyclo)nonan-2-one-3:4-dicarboxylate*, b.p. 188°/8 mm. (the Na derivative of which, with MeI, gives the *Et 3-methyl-3:4-dicarboxylate*, b.p. 174°/7 mm.), hydrolysed to the 4-carboxylic acid, m.p. 136° (*semicarbazone*, m.p. 220°). The *Et* ester, b.p. 143–144°/8 mm. (*semicarbazone*, m.p. 159°), of this with MgMeI gives 2- α -hydroxymethyl-4- α -hydroxyisopropyl-(0:3:4-dicyclo)nonane, b.p. 154°/4 mm., which yields (I) when heated with Se. A. LI.

Teresantalic and isoteresantalic acid. H. STEIGER and H. RUPE (Helv. Chim. Acta, 1937, 20, 1117–1146).—Conversion of *Me teresantalate* into its hydrobromide and removal of HBr by NH_2Ph followed by fractional distillation of the product gives *Me isoteresantalate* (I), b.p. 91.2°/10 mm., $[\alpha]_D^{20} -133.46^\circ$, hydrolysed to homogeneous *isoteresantalic acid* (II), m.p. 137°, b.p. 141–143°/16 mm., $[\alpha]_D^{20} -150.82^\circ$ in C_6H_6 . Examination of the more volatile ester fractions discloses the presence of esters other than those derived from *teresantalic acid* or (II). The residue from the distillation of crude (I) contains unstable esters which are hydrolysed to (II) and an acid of higher m.p., the Semmler-Bartlett lactone (III) identified by hydrolysis to *apoborneolcarboxylic acid*, and a viscous yellow liquid, b.p. 196–204°/10 mm., which is not homogeneous but is converted by HCl or HBr in Et_2O into compounds, $\text{C}_{17}\text{H}_{24}\text{O}_2\text{NCl}$

(IV) and $C_{17}H_{24}O_2NBr$, m.p. 194° and 203° , respectively. The corresponding *base* (V), m.p. 45° , gives an *Ac* derivative, m.p. 120° . Treatment of (IV) with boiling KOH-MeOH gives (V) and a compound, m.p. 134° . Similar treatment of the fraction b.p. $203^\circ/10$ mm. gives the compound $C_{16}H_{19}ON$, m.p. 85° , of Rupe and Tomi (A., 1917, i, 138) and an acid, $C_{16}H_{21}O_2N$, m.p. 168° . Treatment of somewhat impure (I) with $Hg(OAc)_2$ in $AcOH-H_2O$ gives the *acetomercuri*-compound (VI), m.p. 214° (corresponding *chloromercuri*-derivative, $C_{11}H_{14}O_3Cl_2Hg_2$, incipient softening, 160°), converted by NaOH and Zn powder in boiling EtOH into homogeneous (II); the OH-acid, $C_{10}H_{16}O_3$, m.p. about 205° , and the Müller lactone, $C_{10}H_{14}O_2$, m.p. 103° , are also produced. With Zn and HCl (VI) yields (III) and the corresponding OH-acid, m.p. 192° . Similar treatment of Me *teresantalate* with $Hg(OAc)_2$ affords $HgOAc$, a compound, $C_{12}H_{18}O_5Hg$, m.p. $208-210^\circ$, probably an *acetomercuri*-compound of an *apoborneolcarboxylic acid*, and an oil, converted by Zn and KOH in boiling EtOH into a *ketodihydroteresantalic acid*, m.p. 270° , possibly 1-*cis*-*apocamphorcarboxylic acid*. Oxidation of (II) in alkaline solution by $KMnO_4$ gives a neutral substance, $C_{10}H_{14}O_3$, m.p. 220° , probably a lactone of *apocamphene hydratecarboxylic acid*, a substance, $C_8H_{14}O$, b.p. $67.5^\circ/11$ mm., and a compound, $C_{10}H_{12}O_4$, m.p. 203° ; this gives a salt, $C_{10}H_{12}O_5Ag_2$, decomp. 175° , but is converted by CH_2N_2 in Et_2O into the ester, $C_{12}H_{18}O_5$, b.p. $153^\circ/10$ mm., m.p. 42° , so that its constitution is not established. Similar oxidation of *teresantalic* and gives a dicarboxylic acid, $C_{10}H_{12}O_2$, m.p. 248° [*Me*₂ ester, b.p. $135^\circ/10$ mm.; (*NH*₄)₂ salt, decomp. 208°], and an unidentified substance, $C_{10}H_{12}O_3$, m.p. 189° . Ozonisation followed by methylation of (II) gives an ester, b.p. $128.2^\circ/12$ mm., hydrolysed to an acid, $C_9H_{14}O_4$, m.p. $123-124^\circ$, and an acid, m.p. 157° . Oxidation of (II) with HNO_3 (*d* 1.48) gives (III) and an acid, $C_{10}H_{12}O_5$ or $C_8H_{10}O_4$, m.p. 150° . Hydration of (II) with H_2SO_4 yields (III), converted into *apoborneolcarboxylic acid* (Me ester, b.p. $124^\circ/10$ mm., m.p. $40-41^\circ$). Boiling H_2O converts (II) into *santene* and *Asahina's acid*. Hydrogenation (Ni in EtOH- H_2O at room temp.) of (I) gives *Me dihydroisoteresantalate*, b.p. $90.5^\circ/10$ mm., $[\alpha]_D^{20} +8.02^\circ$, hydrolysed by KOH-MeOH to *dihydroisoteresantalic acid*, m.p. $120-121^\circ$, $[\alpha]_D^{20} +7.03^\circ$. Similar hydrogenation of Na *isoteresantalate* yields a *dihydroisoteresantalic acid*, m.p. $106-107^\circ$, $[\alpha]_D^{20} -25.01^\circ$, whereas in presence of Pd a third *isomeride*, m.p. 118° , $[\alpha]_D^{20} +23.47^\circ$ in C_6H_6 , is produced. H. W.

Polyterpenes and polyterpenoids. CXVI. Oxidation of acetyloleanolic acid by chromium trioxide with opening of the double linking. L. Ruzicka and S. L. COHEN (Helv. Chim. Acta, 1937, 20, 1192-1200).—Repetition of the work of Schicke and Wedekind (A., 1933, 612) and consideration of the results in the light of that of Ruzicka and Hofmann

(A., 1936, 477) lead to the conclusion that oleanolic acid does not give an oxidation product, $C_{25}H_{38}O_6$, containing 2 OH and 2 CO_2H . The assumption of such a product was conducive to the previous constitution with the double linking and CO_2H in ring E and its non-existence allows the formula of Ruzicka *et al.* (A., 1937, II, 202). Oxidation of acetyloleanolic acid by CrO_3 at 80° gives an alkali-sol. substance, m.p. about 235° (corr.), which solidifies above its m.p. and then melts again at $303-304^\circ$ (corr.). Analyses of this "acetylviscolic acid" (I) and the "viscolic acid" (II), m.p. about 290° (corr.), produced by its hydrolysis agree with the formula of Wedekind but the figures differ little from those required for (II) or the lactonedicarboxylic acid (III), $C_{30}H_{46}O_2$, of Ruzicka and the identity of (II) with (III) is shown by its transformation into derivatives of (III) or of the corresponding *iso*-series. (I) is transformed by boiling Ac_2O into the anhydride, $C_{32}H_{46}O_7$, m.p. 306° (corr.), identical with Ruzicka's compound and obtained also from (II). Ac_2O and (II) in C_5H_5N yield (I). Treatment of (II) with CH_2N_2 and then with boiling Ac_2O gives an acetyl-lactone *Me*₂ ester, m.p. $186-187^\circ$ (corr.), closely related to the product, m.p. $203-204^\circ$ (corr.), of Ruzicka and, like it, hydrolysed to the Me H isolactonedicarboxylate, m.p. $300-304^\circ$. H. W.

Polyterpenes and polyterpenoids. CXVIII. Catalytic hydrogenation of the $\alpha\beta$ -unsaturated keto-group in glycyrrhetic acid and in keto- α -amyrin. L. Ruzicka, H. LEUENBERGER, and H. SCHELLENBERG (Helv. Chim. Acta, 1937, 20, 1271-1279).—Of the 4 O of glycyrrhetic acid (I) two are present in CO_2H and one in OH. The absorption spectrum suggests that the fourth O is present in an $\alpha\beta$ -unsaturated keto-group as in ketoacetyloleanolic acid. This view is confirmed by hydrogenation (PtO_2 in cold $AcOH$) of Me glycyrrhetate, which gives *Me deoxyglycyrrhetate* (II), m.p. 248° (corr.) after softening, $[\alpha]_D +108^\circ$ in $CHCl_3$. This is transformed by boiling Ac_2O into *Me acetyldeoxyglycyrrhetate*, m.p. $266-267^\circ$ (corr.), $[\alpha]_D +120^\circ$ in $CHCl_3$, also obtained by hydrogenation of Me acetylglycyrrhetate. (I) is hydrogenated similarly to *deoxyglycyrrhetic acid*, m.p. 330° (corr.), $[\alpha]_D +148^\circ$ in $CHCl_3$, transformed by CH_2N_2 into (II). In all cases 2 H_2 is required and CO is transformed into CH_2 . All the compounds give a pronounced yellow colour with $C(NO_2)_4$ in $CHCl_3$. Hydrogenation of keto- α -amyrin gives α -amyrin as main product apparently without admixture with the β -isomeride. α -Amyrin acetate is similarly obtained from keto- α -amyrin acetate. H. W.

Resins of native [German] conifers, their constituents and changes during the working of wood. H. WIENHAUS [with, in parts, H. RITTER, W. SANDERMANN, H. LAMBRECHT, H. ENGELHARDT, H. H. MÜLLER, R. ECK, K. MÜCKE, and E. ENGELMANN] (Papier-Fabr., 1937, 35, 385-392).—A review. The following appears new. No experimental details are given. The most volatile part (20%) of the oil, *d* 1.332, $[\alpha]_D -53.8^\circ$ in Et_2O , -37° in C_6H_6 , from *Pinus sylvestris*, L., contains *d*- α - and β -pinene, Δ^3 -carene, camphene, and limonene; the oil also contains cadinene, cadalene, alcohols, $C_{15}H_{24}O$ and $C_{15}H_{26}O$, and a hydrocarbon, $C_{12}H_{12}$, m.p. 83° (quinone, m.p.

142°). The resin acid (I), m.p. about 142°, $[\alpha]_D -112^\circ$ (A., 1936, 1385), isomerises to abietic acid (II) when repeatedly crystallised from MeOH; its α rapidly becomes positive in 0.01N-HCl-Et₂O and then slowly slightly negative. Irradiation (ultra-violet) also gives an isomeride, $[\alpha]_D +30^\circ$; it contains some *d*-pimaric acid, since hydrogenation gives tetrahydropimaric acid as well as a *H*₂-acid, m.p. about 185°. Dehydrogenation by Pd-C gives about 80% of retene. The Me ester gives a mono-ozonide, C₂₁H₃₂O₅; mild treatment with KMnO₄ gives an amorphous acid (K salt), the Me ester, (OH)₂C₂₀H₂₉·CO₂Me, m.p. 178°, of which gives unsatisfactory products when isomerised or oxidised. Fairly fresh resin from *Picea excelsa*, Lk., contains $\approx 18.5\%$ of steam-volatile material, including *l*- α - and β -pinene, a little Δ^3 -carene, limonene, verbenone, verbenol, and a tetra-unsaturated diterpene, C₂₀H₃₂, and yields *p*-OH·C₆H₄·CH·CH·CO₂H and an acid, m.p. about 150°, $[\alpha]_D -102.4^\circ$. With 0.01N-HCl the latter acid gives (II) by way of an isomeride, m.p. 152°, $[\alpha]_D +41.7^\circ$; it is not homogeneous, since its cryst. Na salt regenerates an acid, $[\alpha]_D -146.7^\circ$; it gives a *H*₂-acid, m.p. 244° (Me ester, m.p. 184°) and, when oxidised, Pr²CO₂H; when distilled, it yields an acid, m.p. 190°, $[\alpha]_D -42^\circ$, oxidised to an acid, C₂₀H₃₀O₂(OH)₄, m.p. 246°, also obtained from (II). The neutral part of a resin from *Picea excelsa* from North Sweden contained a dextrorotatory, autoxidisable, monocyclic diterpene, C₂₀H₃₂ (H₈-compound), and a doubly unsaturated, tert. alcohol, C₁₅H₂₄O. The turpentine from *Abies pectinata*, D.C., contains α - and β -pinene, camphene, sobrerol, Δ^8 -*n*-pentadecadienal (hydrogenated to *n*-C₁₄H₂₉·OH). 17% of a substance, C₁₇H₃₀O₂, m.p. 62° (contains one ethylenic linking and readily loses 1H₂O), and 37—46% of acids, which crystallise with difficulty and contain *l*-pimaric acid. The turpentine from *Larix europaea*, D.C., contains 14% of volatile material (mostly α -pinene), oxygenated, unsaturated diterpenes, and acids which yield (II). With NaHSO₃, pinene suffers dehydrogenation and ring-fission, yielding cymene, C₁₀H₈ derivatives, borneol, azulenes, etc. Tsugalactone and pinoresinol arise by polymerisation of coniferyl alcohol.

R. S. C.

Lignin. I. T. LIESER and V. SCHWIND (Annalen, 1937, 532, 104—115).—Mixtures of AcOH and Ac₂O with relatively much H₂SO₄ dissolve pine wood almost completely. With less mineral acid acetolysis is much slower and is accompanied by maxima and minima indicating the production of substances which are first sol. and then insol. in alkali. Attempts to use partial acetolysis for the isolation of the components of the cell membrane by continuously withdrawing the acetolysate, diluting it with H₂O, and subjecting it to dialysis proceed non-uniformly chiefly owing to the formation of simple substances such as CH₂O, MeOH, and AcOH. The presence of OMe in all fractions is characteristic. Evidence of the existence of a compound of cellulose (I) and lignin (II) is obtained; this can be dissolved in fuming HCl at low temp. but decomposes into its components at higher temp. The introduction of Cu and treatment with CS₂ are used for the characterisation of OH in (II). Model experiments show that only primary and *sec.* OH

participate in the xanthate reaction; these behave similarly towards Cu(OH)₂-NH₃, which also reacts with vicinal phenolic hydroxyls. With CS₂ and NaOH esterification is incomplete but becomes maximal when strong org. bases, e.g., NEt₄·OH, are used. Under these conditions the results given by the two methods are identical. Comparison of the results afforded by these methods with those based on acetylation and methylation leads to the conclusion that "Cu(OH)₂-NH₃-lignin" contains 6.1% of *sec.* and 4.2% of *tert.* OH. Use of the "Cu(OH)₂ method" for the determination of OH in (II) of the cell membrane and in its components [mannan, (I), (II), and xylan] indicates that an appreciable alteration of the OH content of (I) does not occur during the isolation process.

H. W.

Constituents of pyrethrum flowers. VII. Behaviour of the pyrethrins on hydrogenation. H. L. HALLER and F. B. LAForge. VIII. Presence of a new ester of pyrethrolone. F. B. LAForge and H. L. HALLER (J. Org. Chem., 1937, 2, 49—55, 56—61; cf. A., 1936, 1381).—VII. PtO₂-hydrogenation of an 80% pyrethrin-II concentrate in EtOH is rapid until 4 H are absorbed and then slow, finally stopping by inactivation of the catalyst; removal of the acids formed and addition of fresh catalyst leads to further hydrogenation of the neutral fraction. The products are chrysanthemumdicarboxylic acid Me₁ ester, tetra- and less hexa-hydropyrene (separated as semicarbazones, partly by crystallising and partly by dissolving the H₄-semicarbazone in dil. HCl); the amount of H ester is about 20% > that of the pyrethrines. A 55% pyrethrin-I concentrate hydrogenates similarly to chrysanthemumcarboxylic acid, tetra- and hexa-hydropyrene (more of the latter than in the former case); the amount of acid exceeds that of the pyrethrines by 50%. The amount of acid recovered approx. corresponds with that indicated by the Seil method. Hydrogenation may be a method of analysis.

VIII. Pyrethrin-I semicarbazone cannot be obtained pure and is unstable; hydrolysis gives pyrethrolone, chrysanthemum-carboxylic (I) and -dicarboxylic acid, and 7—8% of an acid (II), m.p. 41°, b.p. 175—185°/0.7 mm., $[\alpha]_D 0$ (*p*-phenylphenacyl, m.p. 107°, and Me ester, b.p. 155°/1 mm.); analysis of the esters indicates C₁₆H₃₀O₂ as formula of (II), but titration indicates a mol. wt. of 290. Hydrogenation of (II) gives a *H*₂-acid, m.p. 53°. Deniges' reagent gives with (II) a colour similar to that with (I); the Ba salt is insol. (II) may be a mixture.

R. S. C.

Plants used by the Indians against snake venom and malaria. E. C. DEGER (Arch. Pharm., 1937, 275, 496—503).—"Chalcupa," *Rauwolfia heterophylla*, contains dodecanedicarboxylic acid, glucosides, saponins, small amounts of tannins, a Ca salt, chalcuparesene, C₁₂H₂₂O₄, m.p. 165° (NO₂-derivative), chalcupine-A, C₁₄H₂₁O₁₂N₃, m.p. 170°, and chalcupasulphine, C₂₂H₁₂₉O₇₁N₁₂S (an additive compound of chalcupine-B, C₁₅H₂₄O₁₁N₆, with, probably, a purine). Inorg. constituents of the plant are detailed; they include much Cl and SO₄, but little Na. Injections and infusions of Chalcupa are curative against snake-bite.

R. S. C.

Saponins. XII. Sapogenin of *Gleditschia horrida*, Makino. S. KUWADA (J. Pharm. Soc. Japan, 1935, 55, 1258—1264).—The sapogenin, $C_{31}(H_{50})O_4$, m.p. 299—300° (decomp.), $[\alpha]_D^{20} +32.51^\circ$ in $CHCl_3$, forms a Me_1 ether, m.p. 230.5°, and a diacetate, m.p. 219°. CH. ABS. (r)

Anthrone derived from barbaloin and iso-barbaloin. J. H. GARDNER and L. JOSEPH (J. Amer. Pharm. Assoc., 1937, 26, 794—796).—Alcin was fractionally crystallised from MeOH and the fractions were hydrolysed with aq. borax. The products were purified, reduced with $SnCl_2$ - Sn -HCl, and acetylated. In all cases, the final product was chrysophanic acid-9-anthranol triacetate. Hence both barbaloin and isobarbaloin yield aloecmodin-9-anthrone on hydrolysis (cf. McDonnell and Gardner, A., 1934, 774). F. O. H.

Pechmann's dye. Mechanism of the formation of products obtained by the action of alkali. P. CHOVIN (Compt. rend., 1937, 205, 565—567).—The pure isomeride (I) of Pechmann's dye (II) is yellow. The action of EtOH-KOH on (I), (II), the yellow acid + $2H_2O$ (III) of Kugel (A., 1898, i, 198) and Bogert and Ritter (A., 1925, i, 255), and the yellow acid + $1H_2O$ (IV) of Dufraisse and Chovin (A., 1934, 1108) affords a red-violet salt + $2H_2O$ (V), which when acidified gives the corresponding acid which loses $1H_2O$ to form (IV). Brief interaction of acid with (V) affords (III) but prolonged interaction affords a colourless dihydrated acid probably identical with that obtained by Bogert and Ritter (A., 1925, i, 255). (V) results from the alkaline hydrolysis of both lactone rings. The restitution of one lactone ring gives (IV); when both lactone rings are reformed simultaneously (I) is formed; when they close successively, (II) is formed. J. L. D.

Chasmanthin. F. WESSELY and K. SCHÖNOL [with, in part, A. MÜNSTER and W. ISEMAN] (Monatsh., 1937, 71, 10—26; cf. Feist, A., 1935, 864).—Chasmanthin (I) (improved prep. from Colombo root), $C_{20}H_{22}O_7$, m.p. 246°, contains one lactone grouping, and with NaOH gives chasmanthin A (II), m.p. 260°, $[\alpha]_D +18.47^\circ$ in C_5H_5N , and chasmanthin B (III), m.p. 170—175° (decomp.), $[\alpha]_D +24.86^\circ$ in C_5H_5N , both isomeric with (I). Acetylation of (I) with Ac_2O affords acetylchmanthin I (IV), m.p. 290° (decomp.), hydrolysed (NaOH) to (III) and a little (II), whilst acetylation with Ac_2O -NaOAc yields acetylchmanthin II (V), m.p. 272°, $[\alpha]_D +30.06^\circ$ to $+29.39^\circ$ in C_5H_5N . Acetylation ($NaOAc$ - Ac_2O or Ac_2O alone) of (II) or (III) affords (V), which does not depress the m.p. of acetylchmanthin (VI), m.p. 272°, $[\alpha]_D +12.65^\circ$ in C_5H_5N (from palmarin and Ac_2O or $NaOAc$ - Ac_2O). Methylation (Me_2SO_4 - $NaOH$ -EtOH) of (II) and (III) gives methylchmanthin A, m.p. 260°, $[\alpha]_D +44.46^\circ$ in C_5H_5N , and methylchmanthin B (VII), m.p. 290°, $[\alpha]_D +44.32^\circ$ in C_5H_5N , respectively, whilst (I), similarly treated, yields non-homogeneous products. Hydrogenation ($Pd-H_2$) of (I) gives hydrochmanthin acid (VIII), m.p. 259°, methylated (Me_2SO_4 - $NaOH$) to a Me ether, m.p. 195°, and esterified (CH_3N_2) to a Me ester, m.p. 180°, $[\alpha]_D -11.23^\circ$ in C_5H_5N (cf. Feist, loc. cit.). Similar hydrogenation of (IV) affords an acid, which

on hydrolysis gives (VIII), whilst (V) yields acetyl-hydropalmaric acid, m.p. 271°, $[\alpha]_D +39^\circ$ to $+37^\circ$ in C_5H_5N , also obtained by hydrogenation of (VI). On hydrogenation (II) and (III) give hydropalmaric acid, whilst (VII) yields hydromethylchmanthin acid, m.p. 252°, $[\alpha]_D +56^\circ$ in C_5H_5N . J. D. R.

Clerodin, m.p. 161—162°.—See A., III, 287.

Arjunetin, $C_{11}H_{18}O_4 \cdot H_2O$, m.p. 215°, and an isomeride, m.p. 165°.—See A., III, 331.

Shonanin acid derivatives.—See A., III, 331.

Pseudoauxin and lumiauxin.—See A., III, 286.

Synthesis of benzfuran-2-carboxylic acid and -2-acetic acid. V. TITOFF, H. MÜLLER, and T. REICHSTEIN (Helv. Chim. Acta, 1937, 20, 883—892).—Isatin is converted into coumarandione, which is condensed with $CH_2Br \cdot CO_2Et$ and NaOEt and then hydrolysed to o-oxalophenoxyacetic acid (I), $CO_2H \cdot CO \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO_2H$, m.p. 198—200° (corr.) (Me_2 ester, m.p. 76—78°). Attempted cyclisation of the acid with Ac_2O - H_2SO_4 yields o- $CO_2H \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO_2H$ and CO whilst the action of NaOH at 100° or 200° does not give the desired result. The ester is cyclised by Na in EtOH and then hydrolysed to benzfuran-1:2-dicarboxylic acid (II), m.p. 259—260° (decomp.), partly decarboxylated at 270° to benzfuran-2-carboxylic acid (III), m.p. 162° (decomp.), also obtained with (I) by the action of Ac_2O and NaOAc on (I) at 170—180°. Treatment of (III) with Cu powder in quinoline at 220—270° gives coumarone. $SOCl_2$ transforms (III) into benzfuran-2-carboxyl chloride (IV), b.p. about 122°/12 mm., m.p. 65°, converted by anhyd. HCN and C_5H_5N in Et_2O into the corresponding cyanide, m.p. 142° (corr.), which is hydrolysed by HCl-AcOH to benzfuran-2-glyoxylamide, m.p. 202—204° (corr.); this is transformed by 2N-NaOH into benzfuran-2-glyoxylic acid (V), m.p. 125—126° [phenylhydrazone, m.p. 194—196° (corr.)]. With boiling NH_2Ph followed by HCl (V) yields a nitrogenous compound, m.p. 116°, in place of the desired aldehyde. (IV) is transformed by CH_2N_2 in Et_2O into 2-diazoacetylbenzfuran (V), m.p. about 118° (decomp.), converted by Ag_2O - NH_3 into benzfuran-2-acetamide, m.p. 190—191°, whence benzfuran-2-acetic acid (VI), m.p. 89—90°. Alternatively (V) is transformed by Ag_2O -EtOH into Et benzfuran-2-acetate, b.p. 140—150°/12 mm., which is hydrolysed to (VI). The influence of (VI) on the growth of plants does not exceed that of benzfuran-1-acetic acid. H. W.

Fission of the coumarone nucleus. T. REICHSTEIN and J. BAUD (Helv. Chim. Acta, 1937, 20, 892—894).—2-Bromobenzfuran reacts with difficulty with Mg, better with Mg-Cu alloy. The product is converted by CO_2 into benzfuran-2-carboxylic acid and mainly into o-acetylenylphenol, b.p. about 98°/12 mm. [p-nitrobenzoate, m.p. 107—108° (decomp.)].

H. W.

Heterocyclic compounds. IV. Coumarins from resacetophenone and ethyl acetoacetate and synthesis of coumarino- γ -pyrones. R. D. DESAI and S. A. HAMID (Proc. Indian Acad. Sci., 1937, 6, A, 185—190, and Current Sci., 1937, 6, 56).—Resacetophenone, $CH_2Ac \cdot CO_2Et$, and $POCl_3$ give

7-hydroxy-6-acetyl-4-methylcoumarin (I) (50% yield) [Ac derivative, m.p. 180° (lit. 172°); *semicarbazone*, m.p. 320°], which is brominated to the 3-*Br*-compound, m.p. 216° (Ac derivative, m.p. 195°), hydrolysed (Na_2CO_3) to 6-hydroxy-5-acetyl-3-methylcoumarilic acid, m.p. 260° (decomp.), and 6-hydroxy-5-acetyl-3-methylcoumarone, m.p. 138° [Ac derivative, m.p. 118°; Me ether, m.p. 94°; *semicarbazone*, m.p. 315° (decomp.)]. 7-Methoxy-6-acetyl-4-methylcoumarin is brominated to the *Br*-, m.p. 165°, and *Br*₂-derivatives, m.p. 207°. (I) and Ac_2O -NaOAc give 3'-acetyldimethyl-4:2'-coumarino-(7:6)- γ -pyrone, m.p. 245°, and 7-hydroxy-8-acetyl-4-methylcoumarin similarly yields 3'-acetyl-4:2'-dimethylcoumarino-(7:8)- γ -pyrone, m.p. 260°, along with substances of m.p. 320° and 300°. F. R. S.

Condensation of aldehydes with malonic acid in the presence of organic bases. IX. Condensation of β -hydroxynaphthaldehyde (2-hydroxy-1-naphthaldehyde). K. C. PANDYA and T. A. VAHIDY (Proc. Indian Acad. Sci., 1937, 6, A, 181—184).— β -Hydroxynaphthaldehyde and $\text{CH}_2(\text{CO}_2\text{H})_2$ condense (preferably in presence of a base) to give 5:6-benzocoumarin-3-carboxylic acid in good yield. F. R. S.

Aluminium chloride, a new reagent for the condensation of β -ketonic esters with phenols. S. M. SETHNA, N. M. SHAH, and R. C. SHAH (Current Sci., 1937, 6, 93—94).—PhOH and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ with AlCl_3 in Et_2O or PhNO_2 give 4-methylcoumarin in 30—40% yield. Similarly *o*-OH $\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ and *o*-OH $\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ give Me 5-hydroxy-6-acetyl-, m.p. 165° (also prepared by Fries transformation of 5-acetoxy-), and 5-hydroxy-6-carbomethoxy-, m.p. 185—186°, decarboxylated to 5-hydroxy-4-methylcoumarin (cf. Limaye and Kelkar, A., 1937, II, 254). Condensation with H_2SO_4 yields the 7-OH-compounds (cf. Agarwal and Dutt, *ibid.*, 299). F. R. G.

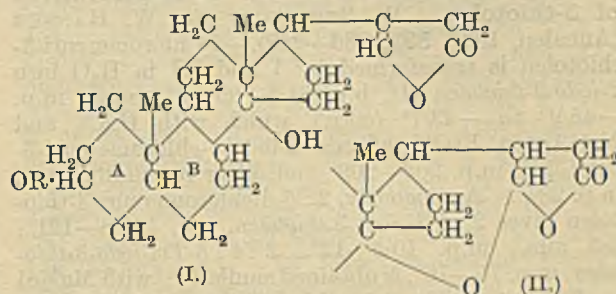
Synthesis of flavonols. Oxidation of flavinodogenides. J. ALGAR and (MISS) I. P. CAREY (Proc. Roy. Irish Acad., 44, B, 37—43).—3-Benzylidene-flavanone is oxidised (KMnO_4 - H_2SO_4) to 3-hydroxy-3-benzoylflavanone (I), m.p. 164—165° (*monoxime*, m.p. 225°), hydrolysed to flavanol and BzOH. With cold Ac_2O (I) gives the *monoacetate*, m.p. 179—180°, but with hot Ac_2O -NaOAc affords a *substance*, $\text{C}_{22}\text{H}_{16}\text{O}_4$, m.p. 135°, hydrolysed to BzOH, flavanol, and other substances. A similar series of reactions yields 3-hydroxy-2-anisoylflavanone, m.p. 153—154° (*monoacetate*, m.p. 157—158°), forming with Ac_2O -NaOAc a *substance*, m.p. 115°; 3-hydroxy-3-(3':4'-methylenedioxybenzoyl)flavanone, m.p. 194—195° (*monoacetate*, m.p. 200—201°), with Ac_2O -NaOAc giving a *substance*, m.p. 148—149°; and 3-hydroxy-3-benzoyl-3':4'-methylenedioxyflavanone, m.p. 196°. F. R. S.

Hydroxydiphenylene oxides.—See B., 1937, 1177.

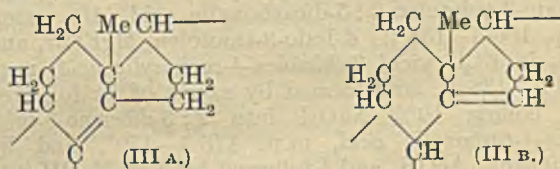
Photolytic production of formaldehyde in the eosin group. E. BAUR and K. GLOOR (Helv. Chim. Acta, 1937, 20, 970—974; cf. A., 1937, II, 28, 318).—Me and Et esters of eosin and Et esters of rhodamines give CH_2O in the Baur-Fricker experiment. Non-

esterified members of the eosin group do not give this effect. H. W.

Constitution of cerberin. T. MATSUBARA (Bull. Chem. Soc. Japan, 1937, 12, 436—441).—Cerberin, new formula, $\text{C}_{29}\text{H}_{44}\text{O}_8$, anhyd. and $+0.5\text{H}_2\text{O}$, m.p. 191—193°, $[\alpha]_D^{25} -77.9^\circ$ in CHCl_3 , from the seed-kernels of *Cerbera Odollam*, Gaertner, is shown to be (I) ($\text{R} = \text{C}_6\text{H}_{11}\text{O}_4$; R *cis* to the Me on C_{10} ; rings A and B *cis*) by the following reactions. It is a heart poison. It neutralises hot, but not cold, alkali, gives Legal's and Baljet's reactions, yields *dihydrocerberin*, $+0.5\text{H}_2\text{O}$, m.p. 185—186°, and is thus a



β -unsaturated lactone. It yields isocerberin (II), m.p. 252—253°, $[\alpha]_D^{20} -73.8^\circ$ in CHCl_3 , which proves the presence of OH on C_{14} . When heated for a long time in 5% H_2SO_4 -EtOH, it gives a methylpentose, cerberose (*osazone*, m.p. 121—122° or, dried at 100°/30 mm., 141—142°, $[\alpha]_D^{21} +62.5^\circ$ in CHCl_3), and a mixture of cerberigenin [(I), $\text{R} = \text{H}$] (not isolated) and anhydrocerberigenin (III A or B), m.p. 220—222°, $[\alpha]_D^{21} +46.8^\circ$



in CHCl_3 (formation of a *digitonide* fixes the position of the OH on C_{10} ; *acetate*, m.p. 175—176°, $[\alpha]_D^{20} +58^\circ$ in CHCl_3). With acid cerberigenin loses H_2O to give (III). Hydrogenation of (III) gives tetrahydroanhydrocerberigenin, m.p. 155—156°, oxidised by CrO_3 to tetrahydroanhydrocerberigenone, m.p. 181—182° (*oxime*, m.p. 210—212°). CrO_3 oxidises (III) to anhydrocerberigenone, m.p. 195—196°, $[\alpha]_D^{20} +74.4^\circ$ in CHCl_3 (*oxime*, m.p. 221—223°). R. S. C.

Action of formaldehyde on ethyl pyromucate. D. DINELLI and G. B. MARINI (Gazzetta, 1937, 67, 417—424; cf. A., 1937, II, 429).—Et pyromucate (I) and paraformaldehyde (II) in H_2SO_4 (*d* 1.84) give a resinous product containing the 5:5'-dicarbethoxy-derivative, m.p. 192° [also obtained from dicarbethoxydifurylmethane and (II)], hydrolysed to the 5:5'-dicarboxy-derivative (III), no m.p. $<280^\circ$, of 3:3'(or 4:4')-dihydroxymethyl-2:2'-difurylmethane internal ether, m.p. 128° [from (III)], hydrogenated (PtO_2 -AcOH) to an H_8 -derivative, b.p. 150°/4 mm. The 5:5'-dicarbethoxy-derivative, m.p. 98°, hydrolysed to the 5:5'-dicarboxy-derivative, m.p. 252°, of α -3:3'(or 4:4')-dihydroxymethyl-2:2'-difurylthane, b.p. 133°/11 mm., is obtained from dicarbethoxy-

difurylthane (*loc. cit.*) and (II), or from (I) and (MeCHO)₃, followed by (II). E. W. W.

Thiophen series. XXXVI. 2-Phenylthiophen-5-carboxylic acid piperidide, a pepper-like substance of the thiophen series. W. STEINKOPF and R. GORDING (*Biochem. Z.*, 1937, **292**, 368—370; cf. A., 1937, II, 163).—5-Iodo-2-phenylthiophen reacts with Mg in presence of EtBr and Et₂O. The solution with CO₂ etc. affords 2-phenylthiophen-5-carboxylic acid, m.p. 184—185° (*acid chloride*, m.p. 80°; *piperidide*, m.p. 103—104°). F. O. H.

Thiophen series. XXXVII. Iodo-derivatives of 3-thiotoluen. W. STEINKOPF and W. HANSKE (*Annalen*, 1937, **532**, 236—249).—2-Chloromercuri-3-thiotoluen is transformed by I and KI in H₂O into 2-iodo-3-thiotoluen (I), b.p. 84.5—85.8°/11 mm., m.p. —45.9° to —43.7° (*corr.*), which with HgCl₂ and NaOAc in EtOH affords 2-iodo-5-chloromercuri-3-thiotoluen, m.p. 208—209° and, after re-solidification, m.p. 284°. Analogously, 2:5-dichloromercuri-3-thiotoluen gives 2:5-di-iodo-3-thiotoluen, b.p. 120.8—121°/2.5 mm., m.p. 10.5—12°. 2:4:5-Tri-iodo-3-thiotoluen, m.p. 75—76°, is obtained similarly; with MgMeI in Et₂O it yields 2:4-di-iodo-3-thiotoluen (II), m.p. 56.5—57.5°, and 4-iodo-3-thiotoluen, b.p. 88°/12 mm., m.p. —25° to —24.5° (*corr.*) [4-iodo-2:5-dichloromercuri-, m.p. 297° (*decomp.*), and -2:5-diacetoxymercuri-, m.p. 235.5° (*decomp.*), -3-thiotoluen]. Treatment of the solution of it and MgEtBr in Et₂O with CO₂ at 0° leads to 4-iodo-3-thiotoluen-2-carboxylic acid, m.p. 208—209° (*K salt*) (whence 4:5-dibromo-3-thiotoluen-2-carboxylic acid, m.p. 225.5—226.5°), and 4-iodo-3-thiotoluen-2:5-dicarboxylic acid (*Me₂ ester*, m.p. 156.5—158°). 4-Iodo-3-thiotoluen, MgEtBr, and CO₂ in Et₂O yield 3-thiotoluen-4-carboxylic acid, m.p. 136.5—138.5°, transformed by excess of Br followed by boiling 10% NaOH into 2:5-dibromo-3-thiotoluen-4-carboxylic acid, m.p. 178.5—179°, and by Hg(OAc)₂, AcOH, and I followed by NaI-NaOH into 2:5-di-iodo-3-thiotoluen-4-carboxylic acid, m.p. 181—183° (*K salt*). The successive action of Mg and CO₂ on (I) affords 3-thiotoluen-2-carboxylic acid, m.p. 143—145°, the *Me ester*, b.p. 116—117.5°, of which is converted into 4:5-di-iodo-3-thiotoluen-2-carboxylic acid (III), m.p. 264.5° (*corr.*) (*Me ester*, m.p. 157—158°), and 5-iodo-3-thiotoluen-2-carboxylic acid, m.p. 178—179.5° (*Me ester*, m.p. 84—86°). 4:5-Dibromo-3-thiotoluen-2-carboxylic acid, m.p. 228—229.5°, and its *Me ester*, m.p. 102—103°, are described. Treatment of (III) with Hg(OAc)₂ in boiling AcOH and of the product with 10% NaCl followed by 10% HCl gives 4:5-di-iodo-3-thiotoluen, b.p. 98.5°/0.5 mm., m.p. 15.7—17.2°, whence 2:3:2':3'-tetraiodo-4:4'-dimethyl-5:5'-mercuridithienyl, C₁₀H₆I₄S₂Hg, m.p. 290° (*decomp.*), 4-iodo-3-thiotoluen-5-carboxylic acid, m.p. 215—218° [*Me ester* (IV), m.p. 75.5—76.5°], and *Me 2-bromo-4-iodo-3-thiotoluen-5-carboxylate*, m.p. 75.5—76.5°. Hg(OAc)₂ and I in AcOH transform (IV) into *Me 2:4-di-iodo-3-thiotoluen-5-carboxylate*, m.p. 112—112.5° [*corresponding acid*, m.p. 240.5—242° (*decomp.*)]. 2:4-Di-iodo-3-thiotoluen-5-carboxylic acid and Hg(OAc)₂ in boiling AcOH yield 2:4-di-iodo-5-acetoxymercuri-3-thiotoluen, m.p. 218—220° (*decomp.*), transformed by NaCl followed by

HCl into (II), which gives 2:4-di-iodo-5-chloromercuri-3-thiotoluen, m.p. 228—229°. 5-Iodo-3-thiotoluen, b.p. 86.5—87.5°/12 mm., m.p. —61° (*corr.*), gives 5-iodo-2-chloromercuri-3-thiotoluen, m.p. 217° when rapidly heated and, after re-solidification, m.p. 282°. The decarboxylation of 5-bromothiophen-2-carboxylic acid and of 3:4:5-tribromothiophen-2-carboxylic acid is described. In all cases the m.p. of the I-derivatives become lower as the lability of the I atoms increases. The reactivity of I in the 2-thiotoluen increases in the sequence 4 → 3 → 5 and in the 3-thiotoluen in the order 4 → 2 → 5. 2:5-Di-iodothiophen is exceptional. H. W.

Thiophen series. XXXVIII. Chloro-derivatives of thiophen and the limited applicability of the method of mixed m.p. among isomeric thiophen derivatives. W. STEINKOPF and W. KÖHLER (*Annalen*, 1937, **532**, 250—282).—Chlorination of thiophen invariably results in the production of mixtures of Cl-derivatives, the separation of which is very difficult on account of the close proximity of their b.p. The homogeneity of the materials is doubtful and they have therefore now been prepared by individual chemical methods. Frequently different compounds of similar m.p. in the thiophen series do not exhibit a depression of the m.p. when mixed. This occurs only with tri- and tetra-substituted thiophens and is favoured by the presence of three Cl, sometimes by two or three Br, but never by several I. Frequently the pairs of substances are shown to be completely isomorphous and to give identical absorption spectra in the ultra-violet. Distinction can be made by irradiation with ultra-violet light, when isomerides with the differentiating atom or group in the α-position give intense, bright colours whereas dull or different shades are obtained when it is in the β-position. Depression of the m.p. is not observed when 2- or 3-nitrothiophen or thiophen-2-sulphonyl chloride is mixed with the corresponding Se derivatives. Similar relationships are not observed in the C₆H₄ series. Crude 2-chlorothiophen (I) is transformed into 2-chloro-5-chloromercurithiophen (II), m.p. 223—224°, which when distilled with 10% HCl gives the homogeneous halide, b.p. 127—128.3° (*corr.*), m.p. —70° to —69°. I and KI convert (II) into 2-chloro-5-iodothiophen, b.p. 95—96°/14 mm., m.p. —25° to —24° (*corr.*). Treatment of (I) with Hg(OAc)₂ in boiling AcOH gives 2-chloro-3:4:5-triacetoxymercurithiophen, whence 2-chloro-3:4:5-trichloromercurithiophen, which gives 2-chloro-3:4:5-tri-iodothiophen, m.p. 126°. Br converts (I) into 2-chloro-3:4:5-tribromothiophen, m.p. 91°; 2-chlorothiophen-5-sulphonyl chloride is obtained by the successive action of ClSO₃H at —10° and PCl₅ on (I). The dichlorothiophen fraction when treated with Hg(OAc)₂ and NaCl affords 2:5-di-chloro-3:4-dichloromercurithiophen, m.p. 314—315°, whence 2:5-dichlorothiophen, b.p. 161—162° (*corr.*), m.p. —43.4° (*corr.*). 2:5-Dichloro-3:4-di-iodothiophen, m.p. 83°, 2:5:2':5'-tetrachloro-3:3'-di-iodo-4:4'-mercuridithienyl, m.p. 238°, 2:5-dichloro-3:4-dibromothiophen, m.p. 65°, and 2:5-dichloro-3-acetothienone, m.p. 39°, are described. 2:5-Dichloro-3:4-di-iodothiophen is transformed by MgEtBr

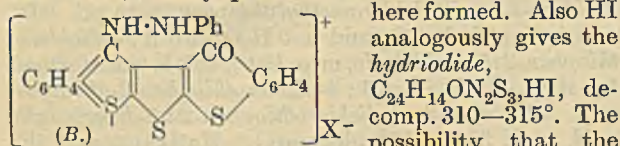
followed by CO_2 in Et_2O into 2:5-dichlorothiophen-3:4-dicarboxylic acid. The trichlorothiophen fraction, b.p. 203—207°, gives with $\text{Hg}(\text{OAc})_2$ in AcOH 2:3:5:2':3':5'-hexachloro-4:4'-mercuridithienyl, m.p. 242—243°, converted by HgCl_2 in COMe_2 into 2:3:5-trichloro-4-chloromercurithiophen, m.p. 211—212° (corresponding 4-bromomercuri-compound, m.p. 207°), whence 2:3:5-trichlorothiophen, b.p. 207.7—209.2° (corr.), which gives 2:3:5-trichloro-4-bromothiophen, m.p. 50.5—51°. 2:3:5-Trichloro-4-iodothiophen has m.p. 51°. The chlorothiophen fraction, b.p. 205—207°, and AcCl with AlCl_3 in light petroleum give 2:3:5-trichloro-4-acetothienone, m.p. 80°, in very small yield. Treatment of crude trichlorothiophen with conc. H_2SO_4 and conc. HNO_3 at 0° leads to 2:3:5-trichloro-4-nitrothiophen, m.p. 70°. 2:5-Dibromo-3-iodo-4-thiophenic acid is transformed by Cl_2 in distilling AcOH into 2:3:5-trichloro-4-thiophenic acid, m.p. 176—177°. 2:3:5-Trichlorothiophen-4-sulphonyl chloride has m.p. 57—58°. Tetrachlorothiophen is treated with MgEtBr in Et_2O and the crude Cl_3 -derivative is converted by HgCl_2 and NaOAc in EtOH into 2:3:4-trichloro-5-chloromercurithiophen, m.p. 211° [whence 2:3:4-trichlorothiophen, b.p. 209.2—210.2° (corr.), m.p. -0.5°], and by $\text{Hg}(\text{OAc})_2$ in boiling AcOH into 2:3:4:2':3':4'-hexachloro-5:5'-mercuridithienyl, m.p. 242—243°, whence 2:3:4-trichloro-5-bromomercurithiophen, m.p. 207°. 2:3:4-Trichloro-5-iodothiophen, m.p. 50—51°, 2:3:4-trichloro-3-bromothiophen, m.p. 50.5°, 2:3:4-trichloro-5-acetothienone, m.p. 80°, 5-nitrothiophen, m.p. 70°, and -thiophen-5-sulphonyl chloride, m.p. 55—56°, are obtained in the usual manner. Cl_2 and 2:3-dibromo-3-thiophenic acid in boiling AcOH give 2:3-dichloro-5-thiophenic acid, m.p. 196—197°, which is converted by $\text{Hg}(\text{OAc})_2$ in boiling AcOH into 2:3-dichloro-4:5-diacetoxymercurithiophen, whence 2:3-dichloro-4:5-dichloromercurithiophen, which when distilled with dil. HCl gives 2:3-dichlorothiophen (II), b.p. 173—174° (corr.), m.p. -26.2° (corr.). This gives 2:3-dichloro-5-chloromercurithiophen, m.p. 269—270°, whence 2:3-dichloro-5-iodothiophen, m.p. 27°. 2:3-Dichloro-5-bromothiophen, b.p. 212—214°, m.p. 6°, 2:3-dichloro-5-acetothienone, m.p. 68°, 2:3:2':3'-tetrachloro-5:5'-dibromo-4:4'-mercuridithienyl, m.p. 238—239°, 2:3-dichloro-5-nitrothiophen, m.p. 55—56°, and 2:3-dichlorothiophen-5-sulphonyl chloride (III), m.p. 55—56°, are obtained in the usual manner. 2:3-Dichloro-4:5-di-iodo-, m.p. 72°, and -4:5-dibromo-, m.p. 67.5°, -thiophen are described. Hydrolysis of (III) with boiling NaOH and treatment of the hydrolysate with Na-Hg in a current of steam gives 3-chlorothiophen (IV), b.p. 136—137° (corr.), m.p. -62°, whence 3-chloro-2-chloromercurithiophen, m.p. 137—138°, 3-chloro-2:5-dichloromercurithiophen, decomp. 275°, and 3:3'-dichloro-2:2'-mercuridithienyl, m.p. 174—175°. The successive action of MgEtBr and CO_2 on (II) affords 3-chloro-2-thiophenic acid, m.p. 175—176°. (IV) is converted by $\text{Hg}(\text{OAc})_2$ in boiling AcOH followed by I into 3-chloro-2:4:5-tri-iodothiophen, m.p. 121°; 3-chloro-2:4:5-tribromothiophen has m.p. 91°. The residues obtained in the prep. of (IV) are dried, treated with PCl_5 and then with EtOH-KOH , thereby giving 2:4-dichloro-

thiophen, b.p. 174—175° (corr.), m.p. -34°; 2:4-dichloro-3:5-dibromothiophen has m.p. 72°. Passage of Cl_2 through 2:5-dimethylthiophen (V) in CCl_4 and treatment of the product with much Br gives 3:4-dichloro-2:5-di(dibromomethyl)thiophen, m.p. 112°, converted by Cl_2 in boiling CCl_4 into 3:4-dichloro-2:5-di(dichloromethyl)thiophen, m.p. 80°, and by pptd. CuCO_3 and hot H_2O into 3:4-dichlorothiophen-2:5-dialdehyde, m.p. 194°; this is transformed by H_2O_2 - KOH into 3:4-dichlorothiophen-2-aldehyde, m.p. 72°, and 3:4-dichlorothiophen-2:5-dicarboxylic acid, m.p. 314—315° (decomp.). $\text{Hg}(\text{OAc})_2$ and the acid in boiling AcOH yield 3:4-dichloro-2:5-diacetoxymercurithiophen, whence 3:4-dichlorothiophen, b.p. 184.5—185.5° (corr.), m.p. 1°, mercurated to 3:4-dichloro-2-chloromercuri-, m.p. 206—207°, and -2:5-dichloromercuri-, m.p. 347—349° after darkening, -thiophen. The latter substance with I and KI gives 3:4-dichloro-2:5-di-iodothiophen. 3:4-Dichloro-2:5-dibromothiophen, m.p. 75°, and 3:4-dichloro-2-acetothienone, m.p. 56°, are described. 3:4-Dichloro-2-hydroxymethylthiophen-5-carboxylic acid has m.p. 220—221°. 2:4:5-Trichloro-3-thiotolen, b.p. 115—116°/23 mm., m.p. -18° (corr.), is obtained from Cl_2 and the corresponding Br_3 -compound in CCl_4 . 2:4:5-Tri-iodo-3-thiotolen is converted by Cl_2 in CHCl_3 at 0° into 2:2:3:4:4:5:5-heptachloro-3-methyltetrahydrothiophen, m.p. 217—218.5° (decomp.). Drastic chlorination of thiophen or chlorination of 2-thiophenic acid in cold AcOH affords 2:3:3:4:5(or 2:2:3:4:5)-pentachloro-2:3-di-hydrothiophen, b.p. 122—126°/13 mm. Br transforms (V) in CS_2 into 3:4-dibromo-2:5-di(dibromomethyl)-thiophen, m.p. 132°, converted by Cl_2 into 3:4-dibromo-2:5-di(dichloromethyl)thiophen, m.p. 103°. 3:4-Dibromothiophen-2:5-dialdehyde, m.p. 227°, is oxidised by KMnO_4 to 3:4-dibromothiophen-2:5-dicarboxylic acid, m.p. 317—318°. 2:3-Dibromo-5-thiophenic acid is transformed into 2:3-dibromothiophen, b.p. 218.6—219.6° (corr.), m.p. -17.5° (corr.). Exhaustive treatment of 2-thiotolen with $\text{Br-H}_2\text{O}$ leads to tetrabromothiophen, m.p. 115—117°.

H. W.

Thiophen series. XXXIX. Constitution of the salts of the phenylhydrazone of $\alpha\beta\alpha'\beta'$ -thiophenobisthiochromone [bis(benzthio-1:4-pyr-ono-2:3)-2':3':5':4'-thiophen]. W. STEINKOPF (Annalen, 1937, 532, 282—288; cf. A., 1937, II, 164).—Treatment of $\alpha\beta\alpha'\beta'$ -thiophenobisthiochromone (A) with HCl , AcCl , or SOCl_2 in ordinary CHCl_3 (containing EtOH) gives the dihydrochloride, $A, 2\text{HCl}$, m.p. 273° (AcCl or SOCl_2 being hydrolysed by EtOH). The more difficultly hydrolysed BzCl gives the adduct, $2A, 3\text{HCl}$, or if EtOH is removed as far as possible from the CHCl_3 , a mixture of the salts, A, HCl and $3A, \text{HCl}$. All these salts lose HCl when heated and ultimately show the m.p. of A; they are all of the same intensely yellow colour. H_2O hydrolyses them slowly. A and $\text{NH}_2\text{NH}\cdot\text{CH}_2\text{Ph}$ give a benzylhydrazone the perchlorate, decomp. 242—248°, of which closely resembles the phenylhydrazone salt. This observation excludes the quinonoid or quinolide structure of the latter (*loc. cit.*). The possibility of a radical structure is considered. Since direct action of I on the phenylhydrazone gives the tri-iodide, m.p. 119—121°

$C_{24}H_{14}ON_2S_3I_3$, m.p. 120—122° (decomp.), I is added to $AgClO_4$ in C_6H_6 as long as decolorisation persists and the solution of the phenylhydrazone is added; no reaction occurs at room temp. and only a pale blue colour develops at 100°. The perchlorate, decomp. 290—310°, readily produced from the acetate, is not



Thiophen series. XL. Mercury derivatives of thiophen. W. STEINKOPF and A. KILLINGSTAD (Annalen, 1937, 532, 288—293).—Dropwise addition of thiophen (I) to a boiling mixture of $HgCl_2 \cdot NaOAc \cdot H_2O \cdot EtOH$ gives 2:5-dichloromercurithiophen, converted by short treatment with $BzCl$ in $PhNO_2$ into Ph 2:5-chloromercurithienyl ketone, m.p. 244—246°, hydrolysed by superheated steam to Ph 2-thienyl ketone, m.p. 55—57°, and converted by I-aq. KI into Ph 5-iodo-2-thienyl ketone, m.p. 129—130°. If the reaction is protracted, 2:5-dibenzoylthiophen, m.p. 114—115°, is produced. 2:5-Diacetoxymercurithiophen is produced by addition of (I) to $Hg(OAc)_2$ in 50% AcOH at 45° and 2:5-dichloromercuri-3-thiotolen in the same manner as the thiophen derivative. The replacement of all the α -H atoms (and only these) by the action of $Hg(OAc)_2$ and 50% AcOH on thiophen derivatives appears general. Thus are produced 2-bromo-5-acetoxymercurithiophen, m.p. 135°, 5-acetoxymercuri-2-thiotolen, m.p. 133° (identified by conversion into 5-chloromercuri-2-thiotolen), 2:5-diacetoxymercuri-3-thiotolen, decomp. >240°, and 4-bromo-2:5-diacetoxymercuri-3-thiotolen, decomp. >270°. In the case of 2:5-dimethylthiophen the β atoms are replaced with production of 3:4-diacetoxymercuri-2:5-thioxen, decomp. >290°.

H. W.

Thionaphthen-2-acetic acid. E. M. CROOK and W. DAVIES (J.C.S., 1937, 1697—1698).—Thionaphthen (I), $CH_2Br \cdot CO_2Et$ (II), and Cu give thionaphthen-acetic, m.p. 141°, or diacetic acid according to the conditions. $MgMeI$ does not react with (I) in Et_2O , but the $MgBr$ -derivative is obtained by adding 2-bromothionaphthen and MeI to an excess of Mg and with CO_2 gives thionaphthen-2-carboxylic acid [S-dioxide, m.p. 218° (decomp.)], the chloride, m.p. 53—54°, of which affords a diazo-ketone, m.p. about 40° (decomp.), converted by $Ag_2O \cdot EtOH$ and subsequent hydrolysis into thionaphthen-2-acetic acid. $C_{10}H_8$ and (II) give a mixture of acids and a ketone.

H. W.

[Enol-betaines. Derivatives of 3:5-diketo-piperidine.] C. GUSTAFSSON (Ber., 1937, 70, [B], 2165—2166; cf. A., 1937, II, 386).—A reply to Kröhnke and Heffe (*ibid.*, 422).

H. W.

[Enol-betaines. Derivatives of 3:5-diketo-piperidine.] F. KRÖHNKE (Ber., 1937, 70,

[B], 2166).—In reply to Gustafsson (preceding abstract) it is pointed out that enol-betaines are of three types, (1) the colourless compounds of high m.p. described by Benary (A., 1908, i, 600) and allied to those of Gustafsson, (2) the coloured, low-melting, basic methine enol-betaines of the pyridinium series, and (3) the benzoylenol-betaines of the pyridinium series which occupy an intermediate position.

H. W.

3-Vinyl-pyridine and -piperidine. H. A. IDDLIS, E. H. LANG, and D. C. GREGG (J. Amer. Chem. Soc., 1937, 59, 1945—1946).—3- α -Hydroxyethylpyridine (Strong and McElvain, A., 1933, 399) is converted by P_2O_5 (in xylene) or $SOCl_2$ (followed by $EtOH \cdot KOH$) into 3-vinylpyridine (hydrochloride, m.p. 114—115°; picrate, m.p. 143—144°; platinchloride, m.p. 158—160°; aurichloride, m.p. 138—140°; mercurichloride, $C_7H_7N \cdot HgCl_2$, m.p. 145—150°), which polymerises when kept. 3- α -Hydroxyethylpiperidine (*loc. cit.*) is dehydrated [conc. H_2SO_4 , little AcOH, 180° (bath)] to 3-vinylpiperidine (picrate, m.p. 162—164°).

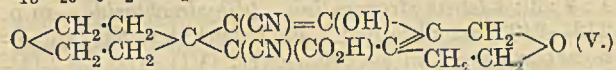
H. B.

Condensation reactions of aldehydes and ketones with ammonia to pyridine bases. Condensations with acetaldehyde and crotonaldehyde. A. E. TSCHITSCHIBABIN (Bull. Soc. chim., 1937, [v], 4, 1826—1831, 1831—1838).—The literature on the formation of C_5H_5N bases from MeCHO or crotonaldehyde (I) with NH_3 is critically reviewed. MeCHO and NH_3 passed over kaolin at 340—360° yield α - (II) and γ - (III) -picoline, 2- and 4-propylpyridine, 2-propenylpyridine, collidinealdehyde (IV), β -collidine (V), and an unidentified collidine (VI) (picrate, m.p. 142°). The bases are separated by fractional distillation and fractional crystallisation of the picrates. (I) and NH_3 similarly yield all the above bases except (VI), and tricrotonylidenetetramine (VII). (MeCHO) $_3$ and aq. NH_3 with NH_4OAc at 160—180° under pressure yield chiefly (IV) with a little (II), (III), and (V), whilst (I), NH_4OAc , and aq. NH_3 at 180° under pressure yield mainly (VII) and a little (IV).

J. D. R.

Quinuclidine. Dicyclo[2:2:2]aza-1-octane. V. PRELOG, D. KOHLBACH, E. CERKOVNIKOV, A. REZEK, and M. PANTANIDA (Annalen, 1937, 532, 69—82).—Quinuclidine (I) is synthesised in good yield, the key intermediate being prepared by four methods. 4-Hydroxymethyltetrahydropyran (improved prep.) and $PBr_3 \cdot C_5H_5N$ give 4-bromomethyltetrahydropyran, b.p. 85—86°/17 mm., and thence tetrahydropyran-4-acetonitrile, b.p. 125—126°/21 mm., and 4-acetic acid (II), b.p. 178°/20 mm., m.p. 54—55°. Tetrahydropyran-4-yl benzenesulphonate, an oil, or, less well, 4-bromotetrahydropyran, b.p. 60—61°/15 mm. (prep. from tetrahydropyran-4-ol by $PBr_3 \cdot C_5H_5N$), with $CH_2(CO_2Et)_2$ gives Et_2 tetrahydropyran-4-malonate, b.p. 156—160°/13 mm., converted into the corresponding acid, m.p. 151°, and thence into (II). Tetrahydro- γ -pyrone (III) with $Zn \cdot CH_2Br \cdot CO_2Et$ gives Et 4-hydroxytetrahydropyran-4-acetate, b.p. 132—140°/15 mm., the Ac derivative, b.p. 140—145°/21 mm., of which, when distilled at 1 atm., gives Et tetrahydropyran-4-ylideneacetate, b.p. 113°/15 mm. (large exaltation of [R]), hydrogenated (PtO_2 ; dry $EtOH$)

to the *Et* ester (IV), b.p. 108—110°/14 mm., of (II). $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, (III), and a trace of piperidine in C_6H_6 give *Et* 4-tetrahydropyran-4-ylidenecyanoacetate, m.p. 66—67° [and, in one experiment, a substance (V), $\text{C}_{18}\text{H}_{20}\text{O}_5\text{N}_2$, m.p. about 260° (decomp.)], hydrolysed



by dil. acid to the corresponding acid, m.p. 137—138°, partly converted by heat into 2 : 3-dihydropyran-4-cyanoacetic acid, b.p. 135°/23 mm., hydrolysed by 20% $\text{H}_2\text{SO}_4\text{--EtOH}$ to *Et* 2 : 3-dihydropyran-4-acetate [by hydrogenation gives (IV)], and converted by $\text{NaOEt}\cdot\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ into *Et* α -cyano- α -(2 : 3-dihydropyran-4- β -p-bromobenzoyl)propionate, m.p. 153—154°. $\text{Na}\cdot\text{EtOH}\cdot\text{C}_6\text{H}_6$ reduction of (IV) gives 4- β -hydroxyethyltetrahydropyran, b.p. 119—120°/14 mm. (phenylurethane, m.p. 70—71°), which with HBr gives α -dibromo- γ - β' -bromoethylpentane, b.p. 185—186°/17 mm., converted by 20% $\text{NH}_3\text{--MeOH}$ at 130—140° into (I), m.p. 158—159° (picrate, m.p. 275—276°). HBr at 100—110° converts (II) into δ -bromo- β - β' -bromoethylvaleric acid, m.p. 71—71.5° the *Me* ester (prep. by CH_2N_2) of which with $\text{NH}_3\text{--MeOH}$ gives *Et* piperidine-4-acetate, b.p. 123—127°/15 mm. [hydrochloride; platinichloride, m.p. 192° (decomp.)], and thence the corresponding acid, m.p. 237—238° (decomp.) [platinichloride, m.p. 210—213° (decomp.); PhSO_2 derivative, cryst.].

R. S. C.

Synthesis of dicyclo[2 : 2 : 3]aza-1-nonane, quinuclidine-2-carboxylic acid, and β -4-piperidylpropionic acid. V. PRELOG and E. CERKOVNIKOV (Annalen, 1937, 532, 83—88).—4-Bromomethyltetrahydropyran and $\text{CHNa}(\text{CO}_2\text{Et})_2$ give *Et* 4-tetrahydropyran-4-ylmethylmalonate, b.p. 166—169°/13 mm., the corresponding acid, m.p. 114—115° (decomp.), from which, when heated, yields β -4-tetrahydropyran-4-ylpropionic acid (I), m.p. 92—93°. The *Et* ester, b.p. 134—139°/17 mm., of this acid with $\text{Na}\cdot\text{EtOH}\cdot\text{C}_6\text{H}_6$ gives 4- γ -hydroxypropyltetrahydropyran, b.p. 143—145°/20 mm., converted by HBr at 100° into α -dibromo- γ - β' -bromomethylhexane, b.p. 204°/21 mm. Yields in these reactions are good. The Br_3 -compound with $\text{NH}_3\text{--MeOH}$ at 130—140° gives 11.8% of dicyclo[2 : 2 : 3]aza-1-nonane, m.p. 129° (platini-, m.p. 238—240°, and auri-chloride, decomp. about 250°; picrate, m.p. 288—289°). HBr and (I) give ϵ -bromo- γ - β' -bromoethylhexoic acid (II) (not obtained pure), the *Et* ester of which with $\text{NH}_3\text{--MeOH}$ affords β -4-piperidylpropionic acid, m.p. 275—276° (decomp.) [hydrobromide, m.p. 220—222°; *Et* ester, b.p. 142—143°/15 mm. (platinichloride, m.p. 190—191°)]. Br -red P at 100° converts (II) into α -dibromo- γ - β' -bromoethylhexoic acid, which with $\text{NH}_3\text{--MeOH}$ gives quinuclidine-2-carboxylic acid, m.p. about 280° (decomp.) [hydrobromide; methochloride, m.p. 298° (decomp.)].

R. S. C.

Nitrogenous heterocyclic rings. XXXIII. Hydrogenation of *o*-phenylenediacetonitrile under high pressure. P. RUGGLI and A. STAUB (Helv. Chim. Acta, 1937, 20, 925—927; cf. A., 1936, 64).—Hydrogenation (Ni in $\text{NH}_3\text{--EtOH}$) of $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{CN})_2$ in a relatively large autoclave so that

there is no considerable fall in pressure of H_2 during the reduction gives *o*- $\beta\beta$ -phenylenediethylamine [*o*- $\beta\beta'$ -diaminodiethylbenzene] (I), b.p. 156—175°/13 mm., in addition to benzo-hexamethyleneimine. (I) yields a methiodide, m.p. 227°, dihydrochloride, m.p. 253°, dipicrate, m.p. 235° (decomp.), and a Bz_2 derivative, m.p. 153°. It resembles the compound of Fries and Bestian (A., 1936, 714) rather than that of von Braun *et al.* (A., 1916, i, 130).

H. W.

Synthesis of 5- and 6-benzoyloxyindoles and attempts to prepare 5- and 6-hydroxyindoles therefrom. H. BURTON and J. L. STOVES (J.C.S., 1937, 1726—1728).—2-Nitro-4-benzoyloxytoluene, m.p. 52°, prepared from 2-nitro-*p*-cresol and CH_2PhCl , with $\text{Et}_2\text{C}_2\text{O}_4$ and KOEt gives 2-nitro-4-benzoyloxyphenylpyruvic acid (+ H_2O), m.p. 89—90°, and 2 : 2'-dinitro-4 : 4'-dibenzoyloxydibenzyl, m.p. 164—165°. The pyruvic acid is reduced [$\text{Fe}(\text{OH})_2$] to 6-benzoyloxyindole-2-carboxylic acid, m.p. 185—186° (decomp.), decarboxylated by heating in glycerol to 6-benzoyloxyindole, m.p. 111—112°. 5-Benzoyloxyindole-2-carboxylic acid (+ H_2O), m.p. 190°, prepared from 2-nitro-5-benzoyloxyphenylpyruvic acid, is decarboxylated to 5-benzoyloxyindole, m.p. 96—97° (1-*Ac* derivative, m.p. 129—130°). Neither 5- nor 6-benzoyloxyindole has been debenzoylated, the products being dark-coloured complex phenolic substances.

F. R. S.

Diethylamides of indole-3-carboxylic, 3-indolylacetic, thionaphthen-2-carboxylic, and reduced 3-indolylacetic acids. R. WEGLER and H. BINDER (Arch. Pharm., 1937, 275, 506—516).— Mg 3-indolyl iodide and $\text{NET}_2\cdot\text{COCl}$ in Et_2O give indolyl-3-carboxyldiethylamide, m.p. 151—151.5° (picrate, m.p. 129.5—120°; *NO*-derivative, m.p. 241—242°, reduced to the $\text{N}\cdot\text{NH}_2$ -derivative, m.p. 177.5—178°; hydrolysed to the known acid), hydrogenated with difficulty to a mixture of H_2 - and H_8 -compounds (picrates, m.p. 182—183.5° and 195—198°). $\text{NET}_2\cdot\text{CH}_2\cdot\text{COCl}$ similarly leads to 3-indolylacetyldiethylamide, m.p. 101° (picrate, m.p. 139—140°; hydrolysed to the known acid), hydrogenated to the 2 : 3- H_2 - [picrate, m.p. 170—172°; additive compound with 2-nitrohydri-dene-1 : 3-dione, m.p. 184° (decomp.)] and H_8 -amide, b.p. 146—147°/0.75 mm. (picrate, m.p. 177—178.5°). Mg 2-thionaphthenyl iodide and $\text{NET}_2\cdot\text{COCl}$ give thionaphthen-2-carboxyldiethylamide, b.p. 220°/11 mm., also obtained from the acid chloride and NHET_2 , and hydrolysed to the known acid. 3-Nitrilindole and $\text{KOH}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ give indole-3-carboxylamide, m.p. 200°. The indollediethylamides could not be obtained by other methods.

R. S. C.

Derivatives of di- and tetra-hydroquinoline.—See B., 1937, 1179.

α -6-Methoxy-8-quinolyl- β -alkylcarbamides. J. W. BOEHMER (Rec. trav. chim., 1937, 56, 901—906).—8-Amino-6-methoxyquinoline is transformed by the necessary alkylcarbimide in PhMe into α -6-methoxy-8-quinolyl- β -alkylcarbamides in which the alkyl is *Me* (I), m.p. 201°, *Et*, m.p. 188°, *Pr*^a, m.p. 197°, *Pr*^b, m.p. 217°, *Bu*^a, m.p. 194°, and *Bu*^b, m.p. 190°. All these compounds afford hydrochlorides. Only (I) appears to have any action on plasmodium relictum.

H. W.

Mechanism of decarboxylation. I. Decomposition of quinaldinic and isoquinaldinic acids in the presence of compounds containing carbonyl groups. P. DYSON and D. L. HAMMICK (J.C.S., 1937, 1724—1726).—When quinaldinic (I) and isoquinaldinic (II) acid are heated with excess of PhCHO, anisaldehyde, and CPhMe, CO₂ is evolved and products are obtained which indicate that the decarboxylation takes place thus: OH·CO·X + COYZ → OH·CXYX + CO₂ where X = quinolyl or isoquinolyl, and Y and Z = aryl, alkyl, or H. (I) with PhCHO gives *phenyl-2-quinolylcarbinol*, m.p. 50—60°, readily oxidised to the ketone, with anisaldehyde forms *anisyl 2-quinolyl ketone*, m.p. 78° (2:4-dinitrophenylhydrazones, m.p. 242°), and with CPhMe yields *phenyl-2-quinolylmethylcarbinol*, m.p. 100°. (II) and PhCHO afford *phenyl-1-isoquinolylcarbinol*, m.p. 106° (Bz derivative, m.p. 158—159°), oxidised (K₂Cr₂O₇) to the ketone. F. R. S.

Iodo-derivatives of substituted phenylquinolinecarboxylic acids.—See B., 1937, 1270.

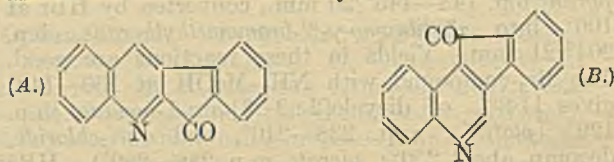
Derivatives of methylcholanthrene and heterocyclic derivatives of cholesterol. W. ROSSNER (Z. physiol. Chem., 1937, 249, 267—274; cf. Dorée and Petrov, A., 1936, 69).—Methylcholanthrene (I) in C₆H₆ gives with conc. HNO₃ in AcOH for 3 hr. at 0° two (NO₂)₂-derivatives, m.p. 224° and 257°, respectively, and with Ac₂O and conc. H₂SO₄ a *monosulphonic acid* (II), m.p. 240° (Me ester, m.p. 274°). In the same way the condensation product (III) of cholestan-3-one and NPh·NH₂ gives a *monosulphonic acid*, m.p. 235° (Me ester, m.p. 190°; K and Na salts). (III) with Se at 320° for 40 hr. gives a *compound* (IV), C₂₉H₃₉N, m.p. 203°; at 340° for 30 hr. (after 16 hr. at 320°) a *compound* (V), C₂₁H₁₇N, probably aminomethylcholanthrene, m.p. 225°; and at 360° (I). Cholestenone with NPh·NH₂ yields a *compound* (VI), C₃₃H₄₇N, m.p. 195°, which with Se gives at 320° a *compound* (VII), C₂₉H₃₇N, m.p. 170°; at 340° for 30 hr. (after 16 hr. at 320°) a *compound* (VIII), C₂₈H₂₇N; and at 360° (I). (II) is not carcinogenic. Formulae are suggested for the compounds (III)—(VIII). W. McC.

Acridine derivatives as antimalarials. U. P. BASU and S. J. DAS-GUPTA (J. Indian Chem. Soc., 1937, 14, 468—473).—5-Chloro-, m.p. 68—69° (cf. A., 1925, i, 65; 1931, 495), with PhOH·KOH at 140° gives 5-phenoxy-, m.p. 102° (hydrochloride, m.p. 223—225°), and with NEt₃·[CH₂]₄·NH₂ (I) and Cu at 150° gives 5-8-diethylaminobutyl-1:2:3:4-tetrahydroacridine (methyleneedioxy-naphthoate, m.p. 216—220°). Et cyclohexanone-2-carboxylate (II) and *p*-anisidine (III) give 7-methoxy-1:2:3:4-tetrahydroacridone, m.p. 295°, which with PCl₅, followed by PhOH at 150°, yields 5-chloro-7-methoxy- (IV), m.p. 122°, and 5-phenoxy-7-methoxy-1:2:3:4-tetrahydroacridine (V), m.p. 120° [hydrochloride, m.p. 220° (decomp.); picrate, m.p. 190—192°]. From (I), (IV), and Cu, or from (I) and (V) (both at 150°), the 7-methoxy-5-8-diethylaminobutyl compound (dihydrochloride, m.p. 193—194°) is obtained. Similarly (IV) gives the 7-methoxy-5-γ-diethylaminopropyl compound (dihydrochloride, m.p. 228—229°). Et 5-methylcyclohexanone-2-carboxylate and (III) yield 7-methoxy-2-methyl-

1:2:3:4-tetrahydroacridone, m.p. 335°, from which 5-chloro-7-methoxy-2-methyl-, m.p. 90°, 5-phenoxy-7-methoxy-2-methyl-, m.p. 103°, 7-methoxy-2-methyl-5-8-diethylaminobutyl- (dihydrochloride, m.p. 203—204°), and 7-methoxy-2-methyl-5-γ-diethylaminopropyl-1:2:3:4-tetrahydroacridine (dihydrochloride, m.p. 242—243°) are obtained. Et 3-methylcyclohexanone-6-carboxylate and *p*-C₆H₄Cl·NH₂ (VI) give Et 2-(4-chloroanilino)-4-methyl-Δ¹-cyclohexene-1-carboxylate, m.p. 90°, which at 270° forms 7-chloro-2-methyl-1:2:3:4-tetrahydroacridone, m.p. 375° (decomp.) (sealed tube), from which (POCl₃-PCl₅) 5:7-dichloro-2-methyl-1:2:3:4-tetrahydroacridine, m.p. 89°, is obtained. Using (II) and (VI), 7-chloro-1:2:3:4-tetrahydroacridone, m.p. 380°, is formed. E. W. W.

3:10-Dihydroxy-1:2:3:4-tetrahydro-7':8'-benzquinoline.—See B., 1937, 1179.

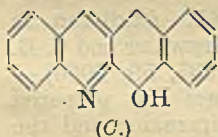
Polynuclear condensed systems with heterocyclic rings. W. BORSCHKE and W. NOLL (Annalen, 1937, 532, 127—145).—Phenylpyruvic acid (I) is transformed by *o*-NH₂·C₆H₄·CHO and NaOH in H₂O-EtOH at 100° into 3-phenylquinoline-2-carboxylic acid (II), m.p. 165° (decomp. into CO₂ and 3-phenylquinoline) (Me ester, m.p. 82°; anilide, m.p. 182—183°). Similarly, (I) condenses with isatin to 3-phenylquinoline-2:4-dicarboxylic acid (III), m.p. 271—272° (decomp.) (Me₂ ester, m.p. 124—125°; dianilide, m.p. 253—255°). Complete decarboxylation of (III) occurs at its m.p. whereas at 210—215° it affords 3-phenylquinoline-4-carboxylic acid (IV), decomp. 277° (Me ester, m.p. 76—77°; anilide, m.p. 222°). 5-Methylisatin and (I) yield 3-phenyl-6-methylquinoline-2:4-dicarboxylic acid, m.p. 281—282° (decomp.) [Me₂ ester, m.p. 131—132°; dianilide (+1H₂O), m.p. 155°], which passes at 220° into 3-phenyl-6-methylquinoline-4-carboxylic acid (V), m.p. 282° (decomp.) (Me ester, m.p. 111—112°; anilide, m.p. 286°), and at 290—295° into 3-phenyl-6-methylquinoline, b.p. 226°/17 mm., m.p. 63—64° (picrate, m.p. 256—257°). Treatment of (II) and (IV) with AlCl₃ in PhNO₂ affords 9-keto-1-aza-2:3-benzofluorene (A), m.p. 190·5°,



and 9-keto-3-aza-1:2-benzofluorene (B), m.p. 238° (picrate, m.p. 227—228°). The dichloride of (III) with AlCl₃ in PhNO₂ gives a mixture of 9-keto-1-aza-2:3-, m.p. 313° (decomp.) (Na salt), and 9-keto-3-aza-1:2- (VI), m.p. 185° (decomp.) and, after resolidification, m.p. about 235° (Na salt; Me ester, m.p. 206—207°), benzofluorene-4-carboxylic acid. Ring-closure by conc. H₂SO₄ at 100° gives (B) from (IV), 9-keto-3-aza-*p*-methyl-1:2-benzofluorene, m.p. 237° [picrate, m.p. 252° (decomp.)], from (V), and (VI) from (III). (A) gives an oxime, m.p. 242—243° (decomp.), and a 2:4-dinitrophenylhydrazones, decomp. 333° (hydrochloride); it is reduced by N₂H₄·H₂O at 100° to 3-aza-1:2-benzofluorene, b.p. 240°/25 mm., m.p. 140°. Reduction with Sn and HCl leads to 1-aza-1:2:3:4-tetrahydro-2:3-benzofluorene, m.p.

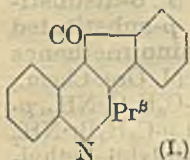
119—122°, and 1-azadihydro-2:3-benzofluorene hydrochloride, m.p. 239—242° after softening at 217°. (B) similarly affords an oxime, m.p. 288°, and a 2:4-dinitrophenylhydrazone, m.p. 315° (decomp.); it is reduced to 3-aza-1:2-benzofluorene, b.p. 242°/14 mm., m.p. 165° [picrate, decomp. 192°; hydrochloride, m.p. 337—338° (decomp.)], or by Sn and HCl followed by acetylation to 3-aza-acetyldihydro-1:2-benzofluorene, m.p. 133—134°, hydrolysed to 3-azadihydro-1:2-benzofluorene hydrochloride, m.p. 293—295°. 3-Aza-*p*-methyl-1:2-benzofluorene, b.p. 246°/12 mm., m.p. 136—137°, gives a hydrochloride, decomp. 343—345°.

Benzylpyruvic acid (VII), α -NH₂·C₆H₄·CHO, and 18% NaOH at 100° yield 3-benzylquinoline-2-carboxylic acid (VIII) (+H₂O), m.p. about 105° and, after re-solidification, decomp. about 133° [hydrochloride (hydrated), m.p. 80—85°, (anhyd.), m.p. 166.5—168.5° (decomp.)]; *Me* ester, m.p. 62°; anilide, m.p. 144°. 3-Benzylquinoline-4-carboxylic acid (IX), m.p. 230.5° (decomp.) (*Me* ester, m.p. 84—85°; anilide, m.p. 244°), is obtained by partial decarboxylation at 200° of 3-benzylquinoline-2:4-dicarboxylic acid, m.p. 188° (decomp.) (or, from AcOH, decomp. 186—188° after softening at 132°; from COMe₂, decomp. 186—188° after softening at 120°; *Me*₂ ester, m.p. 61—63°; dianilide, m.p. 204°), derived from (VII) and isatin; complete decarboxylation at 250° yields 3-benzylquinoline, b.p. 226°/19 mm., m.p. 65—67°. The



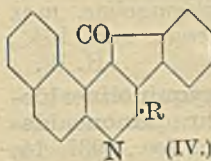
chloride of (VIII) is transformed by AlCl₃ in PhNO₂ into 1-aza-2:3-benzoanthran-9-ol (C), isolated as the Al derivative, (C₁₇H₁₆ON)₃Al, m.p. >360°. Similarly, (IX) gives 3-aza-1:2-benzoanthran-9-ol (X) (hydrochloride, decomp. >360°). Ring-closure with conc. H₂SO₄ appears less satisfactory. (X) gives an *Ac* derivative, m.p. 177—178° [picrate, m.p. 248—249° (decomp.)], and an oxime, m.p. 277—278° (decomp.). Reduction of it with N₂H₄·H₂O does not give a homogeneous material. With glycerol and 82% H₂SO₄ at 150° it gives 7-aza-5:6-benzobenzanthrone, m.p. 255°; it is oxidised by Na₂Cr₂O₇ and 30% H₂SO₄ to 3-aza-1:2-benzoanthraquinone, m.p. 186°, reductively acetylated to 3-aza-1:2-benzoanthraquinol diacetate, m.p. 267° (decomp.). H. W.

Polynuclear, condensed ring systems with heterocyclic rings. II. W. BORSCHKE and F. SINN (Annalen, 1937, 532, 146—165).—COPr³·CH₂Ph, isatin, and KOH in H₂O—EtOH at 100° give 3-phenyl-2-isopropylquinoline-4-carboxylic acid, m.p. 284° (decomp.), the chloride of which is converted by AlCl₃ in



PhNO₂ into 4-isopropyl-3-aza-1:2-benzofluorenone (I), m.p. 184° [picrate, m.p. 233° (decomp.)]; 2:4-dinitrophenylhydrazone, m.p. 275° (decomp.), reduced by N₂H₄·H₂O at about 200° to 4-isopropyl-3-aza-1:2-benzofluorene, m.p. 135°. 2-Chloro-3-phenylquinoline-4-carboxyl chloride similarly affords 4-chloro-3-aza-1:2-benzofluorenone (II), m.p. 214.5° [2:4-dinitrophenylhydrazone, m.p. 322—324° (decomp.)], which does not form a hydrochloride or picrate; it is transformed by N₂H₄·H₂O at 190—200° into 4-hydroxy-

3-aza-1:2-benzofluorene (III), gradual decomp. 330° after becoming discoloured at 300°. 9-Keto-4-methoxy-3-aza-1:2-benzofluorene, m.p. 173° (2:4-dinitrophenylhydrazone, decomp. 328°; oxime, decomp. 240—245°, according to the rate of heating), does not give a hydrochloride or a picrate; it is converted by N₂H₄·H₂O into (III). NaOEt in EtOH and (II) afford 9-keto-3-aza-1:2-benzofluorene, m.p. 238° [picrate, m.p. 226—228°; 2:4-dinitrophenylhydrazone, m.p. 310—311° (decomp.)]. 2-Phenyl-5:6-benzoquinoline-4-carboxyl chloride (corresponding anilide, m.p. 269°) could not be cyclised by AlCl₃ or by conc. H₂SO₄ to the corresponding ketone; the cause does not lie in the inability of the COCl to react since 4-benzoyl-2-phenyl-5:6-benzoquinoline, m.p. 201°, which could not be oximated, is readily produced in presence of AlCl₃ and C₆H₆. 3-Phenyl-5:6-benzo-



quinoline-4-carboxyl chloride and AlCl₃ in PhNO₂ afford 9-keto-3-aza-1:2-1':2'-naphthafluorene [(IV), R = H], m.p. 216° [picrate, m.p. 244°; oxime, m.p. 281° (decomp.)]; 2:4-dinitrophenylhydrazone, m.p. 313° (decomp.)], reduced by N₂H₄·H₂O to 3-aza-1:2-1':2'-naphthafluorene, m.p. 200° (hydrochloride; picrate, decomp. 241° after incipient blackening at about 225°). Phenylpyruvic acid, β-C₁₀H₇·NH₂, and Pr³CHO in boiling EtOH give 3-phenyl-2-isopropyl-5:6-benzoquinoline-4-carboxylic acid, m.p. 277° [decomp. into CO₂ and 3-phenyl-2-isopropyl-5:6-benzoquinoline, m.p. 124°]; picrate of the *Me* ester, m.p. 202° (decomp.) after becoming discoloured], transformed into 9-keto-4-isopropyl-3-aza-1:2-1':2'-naphthafluorene [(IV), R = Pr³], m.p. 161° [picrate, m.p. 192—193°; oxime, m.p. 226° (decomp.)]; 2:4-dinitrophenylhydrazone, m.p. 297° (decomp.)], reduced to 4-isopropyl-3-aza-1:2-1':2'-naphthafluorene, m.p. 202° [picrate, m.p. 216° (decomp.)]. 2:3-Diphenyl-5:6-benzoquinoline-4-carboxylic acid (*Me* ester picrate, m.p. 232°) is transformed by successive treatments with SOCl₂ and AlCl₃ in PhNO₂ into 9-keto-4-phenyl-3-aza-1:2-1':2'-naphthafluorene [(IV), R = Ph], m.p. 211° [picrate, m.p. 249°; oxime, m.p. 242° (decomp.)]; 2:4-dinitrophenylhydrazone, m.p. 293° (decomp.)], whence 4-phenyl-3-aza-1:2-1':2'-naphthafluorene, m.p. 234° (picrate, decomp. 228°). CH₂Bz·CO₂Et, α-NH₂·C₆H₄·CHO, and NaOH slowly and at room temp. afford 2-phenylquinoline-3-carboxylic acid, m.p. 229° (anilide, m.p. 180.5°), the chloride of which is cyclised by AlCl₃ in PhNO₂ to 4-aza-9-keto-2:3-benzofluorene, m.p. 175.5° [picrate, m.p. 198.5°; 2:4-dinitrophenylhydrazone, m.p. 301° (decomp.)], whence 4-aza-2:3-benzofluorene, decomp. 230—235° after becoming discoloured. This yields 9-benzylidene-4-aza-2:3-benzofluorene, m.p. 245—246° (decomp.), and 9-ethoxyl-4-aza-2:3-benzofluorene, m.p. 233—234° (decomp.) (oxime, decomp. 199°; *Bz* derivative, m.p. 167—168°). CH₂(CO₂Et)₂ and α-C₆H₄·Bz·NH₂ at 195—180° give *Et* 2-hydroxy-4-phenylquinoline-3-carboxylate, m.p. 274°, hydrolysed by conc. HCl to the corresponding acid, m.p. 283° (decomp.); this with SOCl₂ yields 2-chloro-4-phenylquinoline-3-carboxyl chloride (*Me* 2-chloro-4-phenylquinoline-3-carboxylate, m.p. 127—128°, cyclised to

1-chloro-9-keto-2-aza-3:4-benzofluorene, m.p. 215—217° (2:4-dinitrophenylhydrazones, decomp. 317°). $\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, and 10% NaOH-MeOH at 100° yield 2-phenylquinoline-3-acetic acid, m.p. 191° (evolution of CO_2 and production of 2-phenyl-3-methylquinoline) [picrate, m.p. 215° (decomp.); Me ester, m.p. 88—89°], the ring compound, m.p. 367—370° (decomp.), from which contains S. Atophan is transformed into the chloride, which with AlCl_3 and C_6H_6 gives 4-benzoyl-2-phenylquinoline, m.p. 114° (picrate, m.p. 213—214°; oxime, m.p. 192—193°; 2:4-dinitrophenylhydrazones, m.p. 245—246°), reduced by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 180° to 4-benzyl-2-phenylquinoline (picrate, decomp. 192°). 2-Chloroquinoline-4-carboxyl chloride, C_6H_6 , and AlCl_3 yield 2-chloro-4-benzoylquinoline, m.p. 105—107° (2:4-dinitrophenylhydrazones, m.p. 247°). 2-Phenylquinoline, AlCl_3 , and BzCl in CS_2 yield 2-p-benzoylphenylquinoline, m.p. 126° (hydrochloride, m.p. 196°; picrate, m.p. 164°; oxime, m.p. 185°). H. W.

Dyes derived from 8-hydroxyquinolinealdehydes and from 2-hydroxyanthraquinonealdehyde. S. K. RAY (J. Indian Chem. Soc., 1937, 14, 414—416).—7-Aldehyde-8-hydroxyquinoline condenses (HCl) with NPhMe_2 or resorcinol, or (H_2SO_4) with o -hydroxytoluic acid (I), giving leuco-bases, m.p. respectively 177°, 148°, and 250°, oxidised by PbO_2 or $\text{NO}\cdot\text{HSO}_4$ to the carbinols. Condensation (H_2SO_4) with resorcinol or $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2$ yields pyronine dyes, m.p. 80° and 86—87°. The 5-aldehyde gives similar results. 1-Aldehyde-2-hydroxyanthraquinone, when condensed (HCl) with NPhMe_2 , or (H_2SO_4) with $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2$ or (I), and the products oxidised, yields dyes, the first two having m.p. 78° and 135°. A. Li.

Syntheses of pyrazolone derivatives. I. Butyl- and isobutyl-antipyrine. A. GIACALONE (Gazzetta, 1937, 67, 460—463).— $\text{CHBu}^i\text{Ac}\cdot\text{CO}_2\text{Et}$ (new prep. using NaOEt and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in EtOH , followed by Bu^iI) and $\text{NHPh}\cdot\text{NH}_2$ in AcOH give 1-phenyl-3-methyl-, m.p. 118°, which with $\text{MeI}\cdot\text{MeOH}$ yields 1-phenyl-2:3-dimethyl-4-isobutylpyrazolone, m.p. 56°. 1-Phenyl-3-methyl-, m.p. 95—96°, and 1-phenyl-2:3-dimethyl-4-n-butylpyrazolone, m.p. 44—45°, are prepared similarly. E. W. W.

Preparation of glyoxaline derivatives from acyloins. K. BERNHAUER and R. HOFFMANN (J. pr. Chem., 1937, [ii], 149, 321—323).—Butyrolin with PhCHO or CH_2O and $\text{NH}_3\cdot\text{Cu}(\text{OAc})_2$ gives 2-phenyl-4:5-di-n-propyl-, m.p. 175—176° (hydrochloride, m.p. 146—147°), and 4:5-di-n-propyl-glyoxaline, m.p. 65—68° (hydrochloride, decomp. 154—156°), respectively. Acetoin gives similarly 2-phenyl-4:5-dimethyl-, m.p. 242° (hydrochloride, m.p. 116—118°), and 4:5-dimethyl-glyoxaline, m.p. 115—117°, b.p. 125—135°/0.3 mm., respectively. Only the Ph bases crystallise well. R. S. C.

Glyoxaline group. VI. Opening of the benziminazole ring. B. ODDO and (SIGNA.) L. RAFFA (Gazzetta, 1937, 67, 537—543; cf. A., 1933, 285).—The MgBr derivative of benziminazole (I) with AcCl or EtCOCl in Et_2O yields 1-acetyl- (II) and 1-propionyl-benziminazole, which when boiled with the acid chloride give no other product. 1-Benzoyl-

benziminazole with BzCl at the b.p., followed by hot H_2O , yields $o\text{-C}_6\text{H}_4(\text{NHBz})_2$. With Ac_2O followed by hot H_2O , (I) gives $o\text{-C}_6\text{H}_4(\text{NHAc})_2$ (III) and (II); (II) also gives (III). With aq. AcOH at 100°, however, (II) yields (I). E. W. W.

Aliphatic polyamines. VI. J. VAN ALPHEN (Rec. trav. chim., 1937, 56, 1007—1012; cf. A., 1937, II, 302).—Even when an excess of primary amine is present, one mol. of $\text{N}(\text{CH}_2\cdot\text{CH}_2\text{Cl})_3$ reacts with only two mols. of the former to give a derivative of 1-β-aminoethylpiperazine. $\text{N}(\text{CH}_2\cdot\text{CH}_2\text{Cl})_3\cdot\text{HCl}$ (I) is converted by boiling NH_2Ph into 4-phenyl-1-β-anilinoethylpiperazine, m.p. 60°, converted by PhNCS into the compound $\text{NPh}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{CS}\cdot\text{NHPh}$, m.p. 105°, and by BzCl into 4-phenyl-1-β-benzanilidoethylpiperazine, m.p. 91°. (I) and NH_3 in $\text{EtOH}\cdot\text{H}_2\text{O}$ at 100° afford 1-β-aminoethylpiperazine (+ H_2O), b.p. 260—280° (picrate, m.p. about 208°). 4-Methyl-1-β-methylaminoethylpiperazine, b.p. 240—260° (oxalate; picrate, decomp. about 210°), is described. 4-β-Aminoethyl-1-β-aminoethylaminoethylpiperazine, $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot[\text{CH}_2]_2\cdot\text{N}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{N}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$, b.p. 235°/38 mm., gives a H oxalate, decomp. 208°, and picrate, decomp. 208°. Boiling piperidine and (I) afford tri-β-1-piperidylethylamine (picrate, m.p. 194°). H. W.

Derivatives of piperazine. XI. Addition to conjugate systems. II. V. E. STEWART and C. B. POLLARD (J. Amer. Chem. Soc., 1937, 59, 2006).—1:4-Di-(β-aroyle-α-arylethyl)piperazines are prepared (method: A., 1936, 1522) from piperazine and the following derivatives of Ph styryl ketone: 3-Me, m.p. 116—116.5°; 4'-chloro-4-methyl, m.p. 149.2—149.6°; 4'-bromo-3-methyl, m.p. 128.8—129.2°; 4'-chloro-3-methyl, m.p. 125.6—126°; 4'-chloro-4-methoxy, m.p. 152—152.5°; 4'-bromo-4-methyl, m.p. 153—153.5°; 4'-bromo-4-methoxy, m.p. 154.8—155.2°; 3:4'-Me₂, m.p. 165.5—166°; 4'-bromo-3:4-methylenedioxy, m.p. 154.5—155.2°. M.p. are corr. H. B.

Infra-red spectrum and molecular structure of diketopiperazine and tetramethyldiketopiperazine.—See A., I, 495.

Derivatives of pyrazolones and of tetrahydro-diazanaphthalene.—See B., 1937, 1179.

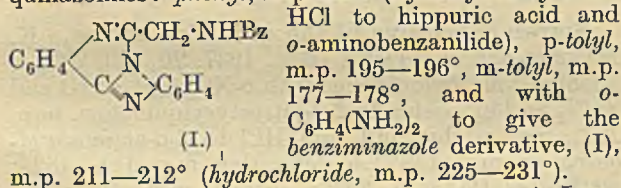
Substituted pyrimidines.—See B., 1937, 1270.

Condensations of aromatic amines with formaldehyde in media containing acid. VI. Use of formic acid in the preparation of 3:6-disubstituted dihydroquinazolines from p-substituted amines, and from their bis(arylamino)methanes and Schiff's bases. E. C. WAGNER (J. Org. Chem., 1937, 2, 157—166).— $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ with CH_2O and HCO_2H give 3-p-tolyl-6-methyldihydroquinazoline and its analogues. These are formed by way of ($p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}$)₂ CH_2 etc., and may also be obtained from the latter, the amine hydrochlorides, and $\text{CH}_2\text{O}\cdot\text{HCO}_2\text{H}$, or from the trimeric Schiff's bases, ($p\text{-C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{CH}_2$)₃, amine, amine hydrochloride, and $\text{CH}_2\text{O}\cdot\text{HCO}_2\text{H}$. The two

latter methods give better yields. The following are described. *NN'*-Methylenebis-*p*-chloroaniline, new m.p. 59–60°; *NN'*-methylenebis-*p*-phenetidine, m.p. 75° (the substance previously regarded as this compound is the trimeric *Schiff's base*, m.p. 90°); *NN'*-methylenebis-*p*-bromoaniline, m.p. 92° [another substance, m.p. 181° (decomp.), was previously so named (cf. A., 1908, i, 534)], which is reduced (Zn-HCl) to *p*-C₆H₄Br·NH₂, *p*-C₆H₄Br·NHMe, and *p*-C₆H₄Br·NMe₂, and is converted by CH₂O into trimeric methylene-*p*-bromoaniline, m.p. 166°; trimeric methylene-*p*-phenetidine, m.p. 90°, similarly reduced to a mixture of amines; 6-methoxy-3-*p*-anisyl-3:4-dihydroquinazoline, m.p. 138° (corr.) [picrate, m.p. 214° (corr.)], hydrogenated to the 1:2:3:4-tetrahydroquinazoline, m.p. 135° (corr.); and 6-ethoxy-3-*p*-phenetyl-3:4-dihydroquinazoline picrate, m.p. 185.5° (corr.). 3-*p*-Tolyl-6-methyl-1:2:3:4-tetrahydroquinazoline and HCO₂H at 150° give the 3:4-dihydroquinazoline.

E. W. W.

Quinazolines. I. T. N. GHOSH (J. Indian Chem. Soc., 1937, 14, 411–413).—1-Keto-3-benzamidomethyl-5:6-benz-2:4-oxazine (Ghosh, A., 1937, II, 393) condenses (Cu powder at 170°) with NH₂Ar to give 1-keto-2-aryl-3-benzamidomethyl-1:2-dihydroquinazolines: *phenyl*, m.p. 205° (hydrolysed by conc.



A. Li.

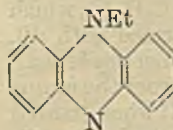
Fission of 2-hydroxy-3-tetrahydroxybutylquinoxalines. II. H. OHLE, W. GROSS, and A. WOLTER (Ber., 1937, 70, [B], 2148–2152; cf. A., 1934, 392).—Fission of these compounds by NPh·NH₂ is not a true hydrolysis but a dehydrogenation. Its incidence is independent of the configuration of the side-chain and of the presence of an electrolytically dissociable OH at C₂. Methylgulonate and *o*-C₆H₄(NH₂)₂ an H₂O at 20° afford 2-hydroxy-3-1-xyloxytetrahydroxybutylquinoxaline, m.p. 170° (decomp.), [α]_D²⁰ –62.0° in H₂O, converted by NPh·NH₂ in boiling H₂O into 2-hydroxyquinoxaline-3-aldehydephenylhydrazine, m.p. 283° (decomp.). 2-Hydroxy-3-*d*-arabotetra-acetoxybutylquinoxaline with CH₂N₂ in CHCl₃ slowly gives 2-methoxy-3-*d*-arabotetra-acetoxybutylquinoxaline, m.p. 154.5–156.5°, [α]_D²⁰ –27.6° in CHCl₃, hydrolysed by NH₃·MeOH at 20° to 2-methoxy-3-*d*-arabotetrahydroxybutylquinoxaline, m.p. 183°, [α]_D²⁰ –13.7° in C₅H₅N, which suffers fission into 2-methoxyquinoxaline-3-aldehydephenylhydrazine, m.p. 145°. The isomeric 2-keto-1-methyl-3-arabotetrahydroxybutyl-1:2-dihydroquinoxaline, m.p. 187°, [α]_D¹⁷ –61.1° in C₅H₅N, is derived from Me glycosonate and *o*-NH₂·C₆H₄·NHMe, HCl, NaOAc, and H₃BO₃ in boiling EtOH. 2-Hydroxy-3-methylquinoxaline is transformed by CH₂N₂ in EtOH into 2-keto-1:3-dimethyl-1:2-dihydroquinoxaline, m.p. 87°. AcCO₂H and *o*-NH₂·C₆H₄·NHMe in presence of AcOH give *pyruv-o*-methylaminoanil, m.p. 139°. 2-Keto-1-methyl-3-dibromomethyl-1:2-dihydroquinoxaline, m.p. 178° (phenylhydrazine, m.p.

198°), is derived from 2-hydroxy-3-dibromomethylquinoxaline and CH₂N₂ in CHCl₃ or from CHBr₂·CO·CO₂H, *o*-NH₂·C₆H₄·NHMe, HCl, and borax in EtOH. H. W.

Phenazine series. V. Reactions of 1:2:3:4-tetrahydrophenazine and related compounds. VI. Reactions of alkyl phenazonium salts; the phenazyls. H. McILWAIN (J.C.S., 1937, 1701–1704, 1704–1711).—V. 1:2:3:4-Tetrahydrophenazine (I) and PhCHO give 1:4-dibenzylphenazine, m.p. 158° [ferrichloride (+AcOH), m.p. 200°], whilst (I) and *p*-NO₂·C₆H₄·CHO yield 1-*p*-nitrobenzyl-3:4-dihydrophenazine, m.p. 172°, and 1:4-bis-*p*-nitrobenzylphenazine, m.p. 250°, reduced to 1:4-bis-*p*-aminobenzyl-1:2:3:4-tetrahydrophenazine, m.p. 176°. According to the time and amounts, (I) and *p*-NMe₂·C₆H₄·CHO give 1-*p*-dimethylamino-3:4-dihydrophenazine, m.p. 158°, or 1:4-bis-*p*-dimethylaminobenzylphenazine, m.p. 207°. 1:2:3:4-Tetrahydrophenazine monomethiodide, m.p. 207°, with NaOH affords 9-methyl-2:3:4:9-tetrahydrophenazine, b.p. 170°/1 mm., and 1:2:3:4:5:6:7:8-octahydrophenazine methiodide, m.p. 175°, similarly gives 9-methyl-2:3:4:5:6:7:8:9-octahydrophenazine, b.p. 160°/1 mm.

VI. Phenazine methosulphate (II) is oxidised in air to a small amount of 2-keto-*N*-methylphenazine, m.p. 200°, also obtained by oxidation of *N*-methyl-dihydrophenazine. *N*-Methylphenazonium hydroxide, presumably the immediate product of the reaction between *N*-methylphenazonium salts and alkalis, is unstable even in absence of air. Under the influence of visible light, these salts oxidise more rapidly, producing mainly the 4-keto-compound, pyocyanine (45 mol. %), phenazine (47 mol. %), and small amounts of 1-hydroxyphenazine and 2-keto-*N*-methylphenazine. NaCN and (II) give *N*-methylphenazyl-2-nitrile, m.p. 145°, and *N*-methyl-dihydrophenazine-2-nitrile, m.p. 155°, which are interconvertible under certain conditions, and both yield phenazine-2-carboxylic acid. Na₂SO₃ and (II) afford *Na H N*-methyl-dihydrophenazinesulphonate (+H₂O), which with K persulphate forms *N*-methylphenazyl- and then *N*-methylphenazonium-sulphonic acid betaine, with Na₂SO₃ giving *Na H N*-methylphenazyl-disulphonate betaine. Phenazine ethosulphate, m.p. 190°, and K₃Fe(CN)₆·NaOH yield 2-keto-*N*-ethylphenazine, m.p. 174°, and with Na₂CO₃ in daylight, 4-keto-*N*-ethylphenazine, m.p. 187°, is obtained. The ethosulphate is reduced (Zn) to *N*-ethyl-dihydrophenazine, m.p. 99°, which with PbO₂ gives *N*-ethylphenazyl (III), m.p. 102°. MeMgI converts (II) into *NN*-dimethyl-*NN*-dihydrophenazine and other products.

F. R. S.



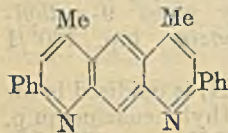
(III.)

azyl (III), m.p. 102°. MeMgI converts (II) into *NN*-dimethyl-*NN*-dihydrophenazine and other products.

Reversible polymerisation as a cause of new types of absorption bands.—See A., I, 494.

Nitrogenous heterocyclic rings. XXX. 4:6-Diamino-1:3-diacetylbenzene and its transformation into derivatives of *lin*-benzodipyrindine. P. RUGGLI and H. REICHWEIN (Helv. Chim. Acta, 1937, 20, 905–913; cf. A., 1937, II, 214).—4:6-Dinitro-*m*-xylene in conc. H₂SO₄ is

oxidised by $\text{CrO}_3\text{--H}_2\text{SO}_4$ at -5° to 4:6-dinitroisophthalic acid, converted by SOCl_2 into the corresponding chloride, m.p. $106\text{--}108^\circ$, which gives a resin with $\text{CHAcNa}\cdot\text{CO}_2\text{Et}$ and could not be transformed into the corresponding cyanide. With CH_2N_2 in Et_2O it affords 4:6-dinitro-1:3-bisdiazoacetylbenzene, decomp. $146\text{--}149^\circ$, in which CO could not be detected and which gives resins when treated with Al-Hg, H_2S , or I. It is transformed by EtOH and conc. HCl into 4:6-dinitro-1:3-dichloroacetylbenzene, decomp. $155\text{--}159^\circ$ after softening at 150° , which cannot be reduced in the usual manner but is converted by Cu in conc. H_2SO_4 at 60° into 4:6-diamino-1:3-dichloroacetylbenzene (I), decomp. about 200° when rapidly heated, which appears to pass in boiling PhNO_2 into an indigoid compound; its Ac_2 derivative, m.p. $175\text{--}176^\circ$ (slight decomp.), and NaOH give a black vat dye. NaI and (I) in cold COMe_2 afford 4:6-diamino-1:3-diiodoacetylbenzene, decomp. $165\text{--}170^\circ$ (indef.). Zn dust and HCl or AcOH transform (I) into 4:6-diamino-1:3-diacetylbenzene (II), m.p. $234\text{--}233^\circ$ (slight decomp.) (Ac_2 derivative, decomp. $240\text{--}245^\circ$).



(III.)

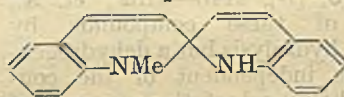
This with COPhMe and KOH-MeOH at 110° gives 2:7-diphenyl-4:5-dimethylbenzodipyrroline (III), decomp. $284\text{--}285^\circ$ [dipicrate, decomp. (indef.) $210\text{--}260^\circ$]. With CH_2Ac_2 and piperidine at $225\text{--}230^\circ$ (II) yields 3:6-diacetyl-2:4:5:7-tetramethylbenzodipyrroline, decomp. $246\text{--}248^\circ$ after darkening at 240° (dipicrate, decomp. 180°). With $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in boiling xylene (II) gives 2:7-dihydroxy-3:6-diacetyl-4:5-dimethyl- or 2:7-diketo-3:6-diacetyl-4:5-dimethyl-1:2:7:8-tetrahydro-benzodipyrroline, decomp. about 415° after slow darkening above 310° . H. W.

Nitrogenous heterocyclic rings. XXXI. Synthesis of indigotin from o-substituted acetophenones. P. RUGGLI and H. REICHWEIN (Helv. Chim. Acta, 1937, 20, 913--918).—Gradual addition of Br in CHCl_3 to an irradiated solution of o- $\text{C}_6\text{H}_4\text{Ac}\cdot\text{NO}_2$ at 50° gives ω -bromo-o-nitroacetophenone (compound, $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}_2\text{Br}$, decomp. $230\text{--}240^\circ$, with $\text{C}_5\text{H}_5\text{N}$), reduced by Cu powder in conc. H_2SO_4 at 50° to ω -bromo-o-aminoacetophenone, m.p. $83\text{--}85^\circ$ (decomp.) after softening at 80° (compound, $\text{C}_{13}\text{H}_{13}\text{ON}_2\text{Br}$, decomp. $210\text{--}223^\circ$, with $\text{C}_5\text{H}_5\text{N}$), which gives very little indigotin (I) when warmed with dil. NaOH in air. ω -Bromo-o-acetamidoacetophenone, m.p. $126\text{--}127^\circ$ after softening at 120° , from the amine and Ac_2O in Et_2O , gives 73% yields of (I) when treated with dil. NaOH and air, thus suggesting the intermediate formation of acetylindoxyl. ω -Chloro-o-nitroacetophenone, from o- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ and CH_2N_2 followed by treatment of the N_2 compound with EtOH- H_2O -HCl, is similarly reduced to ω -chloro-o-aminoacetophenone, m.p. $112\text{--}113^\circ$, which gives only a green colour with aq. NaOH. From ω -chloro-o-acetamidoacetophenone, m.p. $123\text{--}125^\circ$, (I) is obtained in 63% yield. H. W.

Nitrogenous heterocyclic rings. XXXII. Benzodipyrroline derivatives. IV. P. RUGGLI and A. STAUB (Helv. Chim. Acta, 1937, 20, 918--925).—Et₂ m-xylylenedichloromalonate is converted

by conc. $\text{H}_2\text{SO}_4\text{--HNO}_3$ (d 1.5) at 0° into Et₂ 4:6-dinitro-m-xylylenedichloromalonate, m.p. 146° , which when hydrogenated (Ni in EtOH-EtOAc- H_2O) gives Et₂ 2:7-diketo-1:2:3:4:5:6:7:8-octahydrobenzodipiperidine-3:6-dicarboxylate (I), m.p. 252° . Et₂ m-xylylenedimalonate (II) is obtained from m- $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$ and $\text{CHNa}(\text{CO}_2\text{Et})_2$ or by condensing m- $\text{C}_6\text{H}_4(\text{CHO})_2$ with $\text{CH}_2(\text{CO}_2\text{Et})_2$ and piperidine to Et₂ m-phenylenedimethylenemalonate (III), b.p. $265^\circ/11\text{ mm.}$, m.p. 102° , which is subsequently hydrogenated (Ni in EtOAc-EtOH- H_2O). The product gives a mixture of NO_2 -derivatives from which (I) is obtained by reduction. 2:7-Diketo-octahydrobenzodipyrroline-3:6-dicarboxylic acid has m.p. 412° (decomp.). Treatment of (III) with HNO_3 (d 1.5) at 0° yields Et₂ 4-nitro-m-phenylenedimethylenemalonate, m.p. $79\text{--}80^\circ$, reduced to Et₂ 4-amino-m-phenylenedimethylenemalonate, m.p. $172\text{--}175^\circ$ after softening (Ac derivative, m.p. $150\text{--}160^\circ$ after softening at 145°), which is cyclised by EtOH-conc. HCl at 100° to Et₂ 3-carboxycarbostyryl-6-methylenemalonate, m.p. $247\text{--}250^\circ$. m- $\text{C}_6\text{H}_4(\text{CHO})_2$ and barbituric acid in boiling $\text{C}_5\text{H}_5\text{N}$ afford m-phenylenedimethylenemalonate, m.p. $335\text{--}340^\circ$ (decomp.). $\text{CO}(\text{NH}_2)_2$ and (II) with NaOEt in EtOH yield m-xylylenedibarbitoric acid, m.p. $271\text{--}272^\circ$. H. W.

Spiran derivative of the quinoline series. K. MAURER and H. STARCK (Ber., 1937, 70, [B], 2054--2058).—2-Methylquinoline with o- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and ZnCl_2 at 140° yields to 2-o-nitrostyrylquinoline, m.p. 103° , reduced by SnCl_2 and HCl to 2-o-aminostyrylquinoline, m.p. 158° [Ac derivative, m.p. $181\text{--}182^\circ$; methiodide (I), m.p. 233° ; picrate, m.p. 218° ; diperchlorate, decomp. 261° or (+12 H_2O), m.p. 120° ; r-, m.p. 201° , and d-, m.p. 205° , -camphorsulphonate; d-tartrate, m.p. $212\text{--}213^\circ$; Fe^{II} and Fe^{III} salts].



(II.)

Cautious treatment of (I) with KOH-EtOH affords 1-methylspirodihydroquinoline (II), m.p. 115° (picrate, m.p. 233° ; diperchlorate, decomp. $180\text{--}190^\circ$ after becoming black at 150° ; r-, m.p. 218° , and d-, m.p. 230° , -camphorsulphonate; d-tartrate, m.p. 192°), which gives no evidence of mol. asymmetry. It is particularly sensitive to Fe salts, with which it gives a red colour. H. W.

Compound $\text{C}_8\text{H}_{16}\text{H}_4\text{N}_2$, m.p. $256\text{--}257^\circ$, from scollop muscle.—See A., III, 339.

Pyrazoloanthraquinones.—See B., 1937, 1180.

Anthrapyrimidines.—See B., 1937, 1180.

Pyrrole series. III. Relation of tripyrrylmethane cleavage to methene synthesis. A. H. CORWIN and J. S. ANDREWS (J. Amer. Chem. Soc., 1937, 59, 1973--1980; cf. A., 1936, 1122).—Et 2-formyl-4-methylpyrrole-3:5-dicarboxylate (I) (1 mol.), Et 2:4-dimethylpyrrole-3-carboxylate (II) (1 mol.), and dry HCl in C_6H_{14} give 78% of the hydrochloride of 3:5:4'-tricarbethoxy-4:3':5'-trimethylpyrro-methene (III), m.p. 137° (decomp.) (Cu complex), together with some 3:5:4':4''-tetracarbethoxy-4:3':5':3''-5''-pentamethyltri-2-pyrrolymethane (IV); with 2 mols. of (II), the sole product is (IV)

[also formed by fusion of (I) and (II) (2 mols.) at 190–200°]. Contrary to Fischer and Ernst (A., 1926, 621), (IV) undergoes cleavage. Thus, (IV) and HCl in Et₂O–HCO₂H (essential) give 4:4'-dicarbethoxy-3:5:3':5'-tetramethylpyrromethene (V) [together with (III)], whilst (IV), (I), and HCl in Et₂O afford (III). The various reactions which occur with (I)–(IV) can be accounted for on the basis of varying reaction velocities. (III) and cold MeOH–KOH give 3:5:4'-tricarbethoxy-4:3':5'-trimethyl-2-pyrpylcarbinol *Me ether* (VI) (the *Et ether* is similarly obtained using EtOH–KOH), which undergoes the reactions postulated for the free carbinol. Thus, (VI) and HCl in C₆H₁₄ afford (III); (VI), (II), and HCl in C₆H₁₄ yield (IV); (VI), Et 1:2:4-trimethylpyrrole-3-carboxylate (VII), and HCl give (III) and no tripyrrylmethane (cf. below). Fusion of (VI) and (VII) at 145–150° furnishes 3:5:4':4''-tetracarbethoxy-4:3':5':1':3'':5''-hexamethyltri-2-pyrpyl-methane, which according to expectations (cf. above) is cleaved by Et₂O–HCl to (III). Et 2-formyl-1:4-dimethylpyrrole-3:5-dicarboxylate (VIII) and (II) at 190–200° give 3:5:4':4''-tetracarbethoxy-1:4:3':5':3'':5''-hexamethyltri-2-pyrpyl-methane, m.p. 169–170° [also formed from (II), (VIII), and HCl in C₆H₁₄], which is cleaved by HCl to (V) (most rapidly in presence of HCO₂H) and (probably) a 1-methylpyrromethene (not isolated). 3:5:4':4''-Tetracarbethoxy-1:4:1':3':5':1'':3'':5''-octamethyltri-2-pyrpyl-methane, m.p. 178°, is prepared from (VII) and (VIII). Various unidentified products are obtained from (I) and (VII) by fusion or condensation with HCl.

H. B.

Residual affinity and co-ordination. XXXVII. Complex metallic salts containing 2:6-di-2'-pyridylpyridine (2:2':2''-tripyridyl). (SIR) G. T. MORGAN and F. H. BURSTALL (J.C.S., 1937, 1649–1655).—The two forms of 2:6-di-2'-pyridylpyridine (I) (2':2':2''-tripyridyl trihydrochloride tetrahydrate, decomp. 280–285°) are dimorphous (cf. A., 1932, 284) and on oxidation (KMnO₄) give only pyridine-2-carboxylic acid, indicating that it is the central one of the C₅H₅N rings which is preferentially attacked. (I) acts as a tridentate group and furnishes many stable and characteristic co-ordination compounds, divided into two series, which contain severally 1 and 2 mols. of base to each atom of metal. The first series is of type [M tripy X] and [M tripy X]₂, where M = Cu, Ag⁺, Ag⁺, Zn, Cd, Hg, Pd, Pt, and [IrCl₃ tripy]. The second is of type [M 2tripy]X₂ and [M 2tripy]X₃.nH₂O, where M = Fe⁺⁺, Co⁺⁺, Co⁺⁺⁺, Ni, Ru⁺⁺, Os⁺⁺, and Cr⁺⁺⁺. The following are described: 2:2':2''-tripyridyl-cupric chloride dihydrate, -argentous nitrate and perchlorate, -argentic nitrate, chlorate, perchlorate, dithionate, and persulphate, -zinc chloride, -cadmous chloride, -mercuric nitrate, -palladous chloride trihydrate, and -iridium trichloride; bis-2:2':2''-tripyridyl-ferrous bromide tetrahydrate (monohydrate) and iodide monohydrate, -ruthenous chloride tetrahydrate, -osmous chloride tetrahydrate and iodide hydrate, -cobaltous bromide hydrate (+3.5H₂O; monohydrate) and iodide hydrate, -cobaltic chloride heptahydrate, -nickel bromide hydrate (+3.5H₂O; monohydrate,

iodide hydrate, and tartrate tetrahydrate, and -chromic chloride dihydrate.

F. R. S.

Relation between taste and chemical constitution. Naphthoisotriazine group. IV. A. NERI, V, VI. A. NERI and (SIGNA.) G. GRIMALDI. VII–IX. A. NERI (Gazzetta, 1937, 67, 448–453, 453–460, 468–472, 473–476, 477–481, 513–517; cf. A., 1937, II, 433).—IV. 2-Benzene- (I) and 2-p-sulphobenzene-azo- α -naphthylamine-4-sulphonic acid (II) with OMe·C₆H₄CHO in AcOH give *Na* 3-phenyl-2-p-anisyl-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonate (+7H₂O), tasteless, and the Na₂ salt of the corresponding 3-p-sulphophenyl-acid, very sweet. Similarly p-sulphobenzeneazo- β -naphthylamine (III), and benzene- (IV) and p-sulphobenzene-azo- β -naphthylamine-6-sulphonic acid (V) give 2-p'-sulphophenyl-3-p-anisyl-2:3-dihydro-1:2:4-naphthoisotriazine, tasteless, and 2-phenyl-, slightly bitter, and 2-p'-sulphophenyl-3-p-anisyl-2:3-dihydro-1:2:4-naphthoisotriazine-8-sulphonic acid, tasteless.

V. Vanillin gives, from (I) and (II), 3-phenyl-, tasteless, and 3-p-sulphophenyl-2-(4'-hydroxy-3'-methoxyphenyl)-2:3-dihydro-1:3:4-naphthoisotriazine-4-sulphonic acid, slightly salty; from (III), 2-p-sulphophenyl-3-(4'-hydroxy-3'-methoxyphenyl)-2:3-dihydro-1:2:4-naphthoisotriazine, tasteless; and from (IV) and (V), 2-phenyl-, bitter, and 2-p-sulphophenyl-3-(4'-hydroxy-3'-methoxyphenyl)-2:3-dihydro-1:2:4-naphthoisotriazine-8-sulphonic acid, salty with sweet after-taste.

VI. MeCHO gives, from (I) and (II), 3-phenyl-, slightly bitter, and 3-p-sulphophenyl-2-methyl-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonic acid, slightly sweet; from (III), 2-p-sulphophenyl-3-methyl-2:3-dihydro-1:2:4-naphthoisotriazine, tasteless; and from (IV) and (V), 2-phenyl-, bitter, and 2-p-sulphophenyl-3-methyl-2:3-dihydro-1:2:4-naphthoisotriazine-8-sulphonic acid.

VII. CHPh·CH·CHO gives, from (I) and (II), 3-phenyl-, sweet, and 3-p-sulphophenyl-2-styryl-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonic acid, very sweet; from (III), 2-p-sulphophenyl-3-styryl-2:3-dihydro-1:2:4-naphthoisotriazine, tasteless; and from (IV) and (V), 2-phenyl-, tasteless, and 2-p-sulphophenyl-3-styryl-2:3-dihydro-1:2:4-naphthoisotriazine-8-sulphonic acid, tasteless.

VIII. By diazotisation, 1:4-NH₂·C₁₀H₆·SO₃H gives 2- α -naphthaleneazo- α -naphthylamine-4:4'-disulphonic acid (G.P. 42,382), which with PhCHO and other aldehydes gives 2-phenyl-, tasteless, 2-p-anisyl-, sweet, 2-o-hydroxyphenyl-, tasteless, 2-(4'-hydroxy-3'-methoxyphenyl)-, tasteless, and 2-styryl-3-(4'-sulpho- α -naphthyl)-2:3-dihydro-1:3:4-naphthoisotriazine-6-sulphonic acid, sweet. None of the naphthoisotriazines described in the above series has m.p. <300°.

IX. The Na₂ salt of 1-p-sulphobenzeneazo- β -naphthylamine-6-sulphonic acid (prepared in the usual way), with AcOH and aldehydes gives 3-phenyl-, sweet, 3-o-hydroxyphenyl- and 3-p-anisyl-, both tasteless, 3-(4'-hydroxy-3'-methoxyphenyl)-, sweet with salt after-taste, and 3-styryl-2-(4'-sulpho- α -naphthyl)-1:2:4-naphthoisotriazine-8-sulphonic acid, tasteless.

E. W. W.

Cobaltinitrites of hexamethylenetetramine. A. HEMMELER and (SIGNA.) M. ANGELINI (Gazzetta, 1937, 67, 428—434; cf. A., 1936, 303).— $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ and $(\text{CH}_2)_6\text{N}_4$ (I) give the compound, $\text{Na}[(\text{CH}_2)_6\text{N}_4\text{H}]_2[\text{Co}(\text{NO}_2)_6] \cdot 6\text{H}_2\text{O}$. De Koninck's reagent ($\text{CoCl}_2 + \text{NaNO}_2 + \text{AcOH}$, filtered) and (I) give a compound $\text{CoO}[(\text{CH}_2)_6\text{N}_4\text{H}]_4[\text{Co}(\text{NO}_2)_6]_2$.
E. W. W.

Phosphorylation of monoisopropylideneadenosine and of diacetyladenosine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1937, 121, 131—153).—In order to prepare an adenosine-5-phosphoric acid, the OH groups 2 and 3 were blocked as follows. Adenosine and CPh_3Cl in $\text{C}_5\text{H}_5\text{N}$ give a mixture of 5-mono- (I), $[\alpha]_D^{25} -18^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and N:5-di-triphenylmethyladenosine (II), m.p. 200—202°, $[\alpha]_D^{25} -19.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Heating (I) in $\text{C}_5\text{H}_5\text{N}$ with $\text{C}_6\text{H}_4\text{Me} \cdot \text{SO}_2\text{Cl}$ yields N:2:3-tritoluenesulphonyl-5-triphenylmethyl-, $[\alpha]_D^{25} -57.2^\circ$ in COMe_2 , hydrolysed by 80% AcOH to the tritoluenesulphonyl-adenosine, m.p. 195—196°, $[\alpha]_D^{25} -94.4^\circ$ in COMe_2 , the 5 position of which is free since it gives no cryst. derivative with NaI in COMe_2 . With Ac_2O in $\text{C}_5\text{H}_5\text{N}$, (I) yields N:2:3-triacetyl-5-triphenylmethyl-, $[\alpha]_D^{25} +14.0^\circ$ in $\text{C}_5\text{H}_5\text{N}$, hydrolysed by 80% AcOH to 2:3-diacetyl-adenosine, m.p. 181—182°, $[\alpha]_D^{25} -78.7^\circ$ in COMe_2 {also obtained from (II) via 2:3-diacetyl-N:5-di-triphenylmethyladenosine, $[\alpha]_D^{25} -6.0^\circ$ in COMe_2 }, together with acetyl-adenine, m.p. 347—348°. Benzoylation of (I) in $\text{C}_5\text{H}_5\text{N}$ gives N:2:3-tribenzoyl-5-triphenylmethyl-, $[\alpha]_D^{25} -41.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$, hydrolysed by 80% AcOH to 2:3-dibenzoyl-adenosine, m.p. 132—134°, $[\alpha]_D^{25} -107.8^\circ$ in COMe_2 , together with benzoyl-adenine. Adenosine, COMe_2 , and ZnCl_2 yield 2:3-isopropylideneadenosine, m.p. 200—204°, $[\alpha]_D^{25} -99.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Phosphorylation (cf. A., 1935, 1481) of this with 2 mols. of POCl_3 , or of diacetyl-adenosine with 1 mol., and hydrolysis of the product with N-HCl gives adenosine-5-phosphoric acid, isolated as Ba salt.
A. Lr.

Absorption spectra of pyrrole colouring matters. Pyrromethenes and bilirubinoids.—See A., I, 548.

Morpholine alkanols.—See B., 1937, 1179.

Action of xanthhydrol on pyrroles. G. ILLARI (Gazzetta, 1937, 67, 434—439).—Xanthhydrol (I) and pyrroles, in AcOH , give mono- and di-xanthyl-pyrroles. The following are described: 2:5-di-xanthyl-, m.p. 200° (decomp.) (converted by KOH fusion into maleimide and xanthen), 5-xanthyl-2-ethyl-, m.p. 190—191°, 2-acetyl-5-xanthyl-, m.p. 221—224° (decomp.), 5-xanthyl-2:4-dimethyl-, m.p. 218—219° (decomp.), 3-acetyl-5-xanthyl-2:4-dimethyl-, m.p. 253° (decomp.), and 2:5-dixanthyl-1-phenyl-pyrrole, m.p. 256—259° (decomp.). 2:4-Dimethylpyrrole-3:5-dicarboxylic acid, 3:5-diacetyl-2:4-dimethyl-, 2:5-diethyl-, and 2:5-diacetyl-pyrrole do not condense with (I). It is suggested that (I) might be used as a reagent for identifying mixed pyrroles.
E. W. W.

Pharmaceutical applications of furfuraldehyde. I. A. MANGINI (Annali Chim. Appl., 1937, 27, 386—392; cf. A., 1937, II, 428).—Furfuraldehyde and AcCO_2H with *o*-, *m*-, and *p*-toluidine yield

2-2'-furyl-8-, m.p. 248—249° (decomp.) (*Na* salt), 7-, m.p. 272—272.5° (decomp.) (*Na* salt), and 6-methylcinchoninic acid, m.p. 253—254° (decomp.) (*Na* salt), respectively. The acids are more or less active in the elimination of uric acid and are more tolerable and less toxic than atophan derivatives.

L. A. O'N.

Oximinopyrroles. VII. Synthesis of phenyl-benzylfurazan. T. AJELLO (Gazzetta, 1937, 67, 444—448).— $\text{CH}_2\text{Ph} \cdot \text{CBz} \cdot \text{N} \cdot \text{OH}$ and NH_2OH give *Ph CH}_2\text{Ph diketone dioxime*, m.p. 217—218° (*Bz}_2\text{ derivative*, m.p. 146°; *Ni* salt), of which the *Ac}_2\text{ derivative*, amorphous, is converted by boiling 10% KOH into the substance $\text{C}_{15}\text{H}_{12}\text{ON}_2$, m.p. 98—99° (cf. A., 1935, 763; 1937, II, 264), which is thus shown to be 3-phenyl-4-benzyl-1:2:5-oxadiazole.

E. W. W.

Hydroxyquinolines. III. Syntheses of diphenylquinolinoisooxazine and of its *N*-substituted derivatives. F. PIRRONE (Gazzetta, 1937, 67, 529—536).—8-Hydroxyquinoline (I) and $\text{CHPh}(\text{N} \cdot \text{CHPh})_2$ in C_6H_6 at 60° give 2:4-diphenyl-5:6-(7':8'-quinolino)-1:3-isooxazine (II) (A., 1936, 1526). In EtOH at 60°, (I), PhCHO , and $\text{HCO} \cdot \text{NH}_2$, NH_2Ac , NH_2Bz , or *p*-OH-C₆H₄·CO·NH₂ give respectively the 3-formyl-, m.p. 158—159°, 3-acetyl-, m.p. 208—209° (picrate, m.p. 164—165°), 3-benzoyl-, m.p. 198—199° (picrate, m.p. 186°), and 3-salicyl-, m.p. 171—172°, derivatives of (II).
E. W. W.

Action of sulphuric acid on unsaturated thiocarbimides: thiolthiazolines. H. A. BRUSON and J. W. EASTES (J. Amer. Chem. Soc., 1937, 59, 2011—2013).— β -Methylallylthiocarbimide (I), b.p. 64°/10 mm., 169—170°/760 mm. (from $\text{CH}_2\text{CMe} \cdot \text{CH}_2\text{Cl}$ and $\text{MeOH} \cdot \text{NaCNS}$), and aq. 27% NH_3 give β -methylallylthiocarbamide, m.p. 92—94°, which is converted by aq. 35% HCl at 140° into 2-amino-5:5-dimethylthiazoline hydrochloride, m.p. 127—129.5°. 5:5-Dimethylthiazoline-2-diazonium chloride, decomp. violently about 140°, and H_2S in aq. KOH afford 2-thiol-5:5-dimethylthiazoline (II), m.p. 162.5—163° (*Ac*, m.p. 69.5°, *Bz*, m.p. 91°, and *ClHg*-derivatives), also prepared from 2-thiol-5:5-dimethylloxazoline, m.p. 107—109° (from $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ and CS_2 in aq. $\text{EtOH} \cdot \text{KOH}$), and P_2S_5 in C_6H_6 . (II) is also obtained from (I) and 95% H_2SO_4 at <5°; (I) \rightarrow $[\text{CH}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS}_2\text{H}] \rightarrow \frac{\text{CMe}_2 \cdot \text{S}}{\text{CH}_2 \cdot \text{NH}} > \text{CS} \rightarrow$ (II).

β -Methyl- α -ethylallyl alcohol (from MgEtBr and $\text{CH}_2\text{CMe} \cdot \text{CHO}$), SOCl_2 , and $\text{C}_5\text{H}_5\text{N}$ at 65° give the chloride, b.p. 120—124°, and thence β -methyl- α -ethylallylthiocarbimide, b.p. 190—200°/760 mm., converted by 95% H_2SO_4 at 0° into 2-thiol-5:5-dimethyl-4-ethylthiazoline [or 2-thiol-5-methyl-5-propylthiazoline (cf. Billeter, A., 1925, i, 1051)], m.p. 115—118°.

H. B.

Reactions in the thiazole series. I. Reactions of 2-chlorobenzthiazoles with thiocarbamides. WINFIELD SCOTT and G. W. WATT (J. Org. Chem., 1937, 2, 148—156).—2-Chlorobenzthiazole (I) and $\text{CS}(\text{NH}_2)_2$ (II) in EtOH at the b.p. give 2-thiol-benzthiazole. This is also obtained from allyl- (III), phenyl- (IV), and *o*-tolyl-thiocarbamide (V), but not from *s*-diphenyl- (VI), *s*-dicyclohexyl- (VII) [from

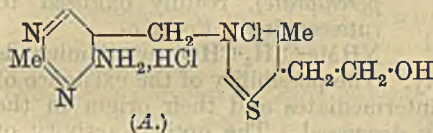
($C_6H_{10}N_2$) CH_2 and S], *N*-phenyl-*N'*-dimethyl- (VIII), or *NN*-pentamethylene-*N'*-phenyl-thiocarbamide. With thiobenzimidazolone, (I) gives an additive compound, $C_{14}H_{10}ClN_3S_2$, m.p. 233–234° (decomp.). 2-Chloro-6-nitrobenzthiazole and (II), (III), (IV), (V), (VI), or (VII) give 2-thiol-6-nitrobenzthiazole (IX), m.p. 225–227°; reaction with (VI) is very slow, whilst with (VII) some *s*-dicyclohexylcarbamide is formed. With (VIII), no (IX) is identified, 6-nitro-2-dimethylaminobenzthiazole, m.p. 197.5–199°, and an unidentified product being formed. In general, thiocarbamides react the less readily as they are the more substituted. 1:1'-Dipiperidinomethane and S in xylene give *piperidine pentamethylenedithiocarbamate*, m.p. 172–173°. E. W. W.

5-Nitrobenzthiazyl dithiocarbarnates.—See B., 1937, 1179.

1-Amino-5:6-tetramethylenebenzthiazole.—See B., 1937, 1179.

Pyrimidylthiazoles.—See B., 1937, 1270.

Synthesis of the antineuritic vitamin. H. ANDERSAG and K. WESTPHAL (Ber., 1937, 70, [B], 2035–2054).



—The constitution A is established synthetically for vitamin-

B_1 (I). γ -Acetopropyl acetate is brominated in anhyd. Et_2O and the crude product is converted by $Ba(CNS)_2$ in $EtOH$ into γ -thiocyano- γ -acetopropyl acetate, isomerised in acid solution to 2-hydroxy-4-methyl-5-acetoxyethylthiazole, m.p. 89°. This is transformed by boiling $POCl_3$ into 2-chloro-4-methyl-3-acetoxyethylthiazole, b.p. 103–105°/0.7 mm., reduced by Zn dust and $AcOH$ at 70° to 4-methyl-5-acetoxyethylthiazole, b.p. 112°/5 mm. (picrate, m.p. 133°), whence 4-methyl-5-hydroxyethylthiazole, b.p. 123–124°/3 mm. (picrate, m.p. 163–164°), identical with the basic product obtained by fission of (I) (Williams, A., 1935, 504, 668). Arising from the suggestions of Williams (*loc. cit.*) and Windaus *et al.* (A., 1936, 253) with regard to the pyrimidine portion of the mol. of (I) the synthesis of 4'-methylthiazolo-3':2'-1:2-benzimidazole, m.p. 165°, from $CH_2Cl \cdot COMe$, thiolbenzimidazole, and Na in $EtOH$ and of 4'-methylthiazolo-3':2'-1:2-5-methyliminazole, b.p. 150–160°/23 mm. (hydrochloride, m.p. 242°), from 2-thiol-4-methyliminazole and $CH_2Cl \cdot COMe$, has been effected. These compounds as bases and salts are colourless and devoid of the fluorescence in the ultra-violet of the thiochrome obtained by the alkaline oxidation of (I). The previous suggestions for the constitution of (I) appear therefore inaccurate in this respect and further progress is made by the synthesis of all possible pyrimidine portions except the known 5:6-diamino-4-ethylpyrimidine. 4-Amino-2:6-dimethylpyrimidine could not be nitrated. Et benzene-azoacetate, acetamide hydrochloride (II), and Na in $EtOH$ afford 5-benzeneazo-4-hydroxy-2:6-dimethylpyrimidine, m.p. 186°, reduced by $Na_2S_2O_4$ and $NaOH$ to 5-amino-4-hydroxy-2:6-dimethylpyrimidine, m.p. 194°. This with PCl_5 in boiling $POCl_3$ affords 4-chloro-5-amino-2:6-dimethylpyrimidine, m.p. 80°

X (A., II.)

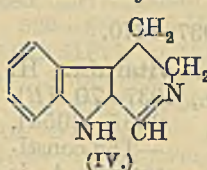
(picrate, m.p. 169°), transformed by $NH_3 \cdot MeOH$ at 238° into 4:5-diamino-2:6-dimethylpyrimidine, m.p. 248° [monohydrochloride (+0.5 H_2O), m.p. 271°; monopicrate, m.p. 235°, condensation product, $C_{20}H_{16}N_4$, m.p. 207°, with benzil], which differs greatly from the degradation product of Windaus. Et_2 formylsuccinate, (II), and $NaOEt$ in boiling $EtOH$ give Et 4-hydroxy-2-methylpyrimidyl-5-acetate, m.p. 179°, whence Et 4-chloro-2-methylpyrimidyl-5-acetate, b.p. 110°/4 mm., m.p. 40–41°, converted by $NH_3 \cdot MeOH$ into 4-amino-2-methylpyrimidyl-5-acetamide, (III), m.p. 250° (corresponding acid, m.p. 270°), and 4-methoxy-2-methylpyrimidyl-5-acetamide (IV), m.p. 201°. Treatment of (III) with Br and KOH and $PhCHO$ successively and hydrolysis of the product with HCl yields 4-amino-2-methyl-5-aminomethylpyrimidine, m.p. 132° [dihydrochloride, m.p. 268–269°; picrate, m.p. 224–225°; sulphate, m.p. 276°; formyl derivative, (V), m.p. 224°], identical with the product of Windaus. P_2S_5 in boiling $PhMe$ transforms (V) into 4-amino-2-methyl-5-thioformamidomethylpyrimidine (VI), m.p. 193°. Treatment of (IV) with Br and KOH gives 4-methoxy-2-methyl-5-aminomethylpyrimidine, b.p. 110–116°/? mm. (picrate, m.p. 188°), the dihydrochloride, m.p. 150–151°, of which is transformed by $NaNO_2$ into 4-amino-2-methyl-5-hydroxymethylpyrimidine, m.p. 194° (hydrochloride, m.p. 224°), whence (HBr in $AcOH$ at 40°) 4-amino-2-methyl-5-bromomethylpyrimidine dihydrobromide, m.p. 213° (decomp.). This with 4-methyl-5-hydroxyethylthiazole at 120–130° gives 4-methyl-5- β -hydroxyethyl-N-4'-amino-2'-methyl-5-pyrimidylmethylthiazolium bromide hydrobromide, m.p. 220°, also obtained by treatment of acetopropyl benzoate, b.p. 138–140°/2 mm., with Br and then with (VI) and identical with vitamin- B_1 hydrobromide. This is transformed through the picrate, m.p. 201–202°, into the corresponding hydrochloride, m.p. 252°, chemically and physiologically identical with the natural material. 2:4-Dihydroxy-6-methyl-5-hydroxymethylpyrimidine and PCl_5 in boiling $POCl_3$ afford 2:4-dichloro-6-methyl-5-chloromethylpyrimidine, b.p. 120°/3 mm., m.p. 39°, which with NaI in $COMe_2$ affords 2:4-dichloro-6-methyl-5-iodomethylpyrimidine, m.p. 90°. This with $AgOAc$ in $COMe_2$ yields 2:4-dichloro-6-methyl-5-acetoxymethylpyrimidine, b.p. 141°/4 mm., m.p. 55°, converted by $NH_3 \cdot EtOH$ at 100° into 2-chloro-4-amino-6-methyl-5-hydroxymethylpyrimidine, m.p. 179°, which with Zn dust in boiling H_2O gives 4-amino-6-methyl-5-hydroxymethylpyrimidine, m.p. 166°. 4-Amino-6-methyl-5-bromomethylpyrimidine hydrobromide (VII), m.p. 210–212°, is condensed with the thiazole derivative at 120–130° to 4-methyl-5-hydroxyethyl-N-4'-amino-6'-methyl-5'-pyrimidylmethylthiazolium chloride hydrochloride, m.p. 242° (corresponding hydrobromide; picrate, m.p. 193°; picrolonate, m.p. 213°). This resembles (I) in giving an intense ultra-violet fluorescence when oxidised by alkaline $K_2Fe(CN)_6$ but is distinguished, *inter alia*, by less physiological activity. $NH_3 \cdot MeOH$ at 100° transforms (VII) into 4-amino-6-methyl-5-aminomethylpyrimidine (VIII) (picrate, m.p. 238°; hydrochloride, m.p. 277°). Et_2 acetosuccinate, $CS(NH_2)_2$, and $NaOEt$ in boiling $EtOH$ afford 4-hydroxy-2-thiol-6-methylpyrimidyl-5-acetic acid, m.p. 295° (Na salt), the Et ester, m.p. 218°, of which is

transformed by $\text{Pb}(\text{OAc})_2$ and H_2O_2 in AcOH at 30–40° into *Et* 4-hydroxy-6-methylpyrimidyl-5-acetate, b.p. 203–205°/0.5 mm., m.p. 153°. This with boiling POCl_3 gives *Et* 4-chloro-6-methylpyrimidyl-5-acetate, b.p. 116–117°/1.5 mm., whence (NH_3 - MeOH at 120–130°) 4-amino-6-methylpyrimidyl-5-acetamide, m.p. 223°, and (VIII). H. W.

Oxidation of benzoylanabasine with potassium permanganate. G. MENSCHIKOV, J. LOSIK, and A. OREKHOV (Chim. Farm. Prom., 1934, No. 6, 7–8).—dl- δ -Benzamido- δ -(3-pyridyl)valeric acid, m.p. 146°, is formed, and, with HCl , yields δ -amino- δ -(3-pyridyl)valeric acid dihydrochloride. CH. ABS. (r)

Synthesis of natural substances, particularly alkaloids, under physiological conditions and its relationship to the question of the formation of vegetable compounds in the cell. C. SCHÖFF [with G. LEHMANN, W. ARNOLD, K. KOCH, H. BAYERLE, K. FALK, F. OECHLER, and H. STEUER] (Angew. Chem., 1937, 50, 779–787, 797–805).—There is no evidence of any spontaneous chemical change in the animal cell. In the vegetable cell the reactions may be important for life and controlled at every stage by a sp. enzyme of the cell or may be accidental whether or not controlled by an enzyme. Far-reaching conclusions can seldom be drawn from the constitution of a single natural product but greater probability is attached to consideration of the "comparative anatomy" of a series of closely related compounds. The hypothetical method of biogenesis is then subjected to the criteria of physiological possibility and inherent probability with regard to initial materials. For the synthesis of the alkaloids of the *Angostura* bark, $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is too feebly reactive to serve as initial material. The condensation of $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ with aldehydes or ketones requires too conc. alkali but its reaction with $\beta\text{-CO-acids}$ at p_H 5–11, best at p_H about 7.0, takes place with loss of CO_2 and leads with suitable partners to quinoline, 2-methyl- and 2-*n*-amylquinoline. Condensation of $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ with $\text{Me}\cdot[\text{CH}_2]_4\cdot\text{CHO}$, $(\text{OMe})_2\text{C}_6\text{H}_3\cdot[\text{CH}_2]_2\cdot\text{CHO}$, and $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot[\text{CH}_2]_2\cdot\text{CHO}$ is suggested for the biogenesis of the 4-hydroxyquinoline derivatives. Condensation of succindialdehyde (I) with NH_2Me and $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ leads directly at p_H 3–11 to tropinone, whereas at p_H 13 tropinone-dicarboxylic acid results. The alkaloids derived from tropinonecarboxylic acid may owe their origin to the condensation of (I) with NH_2Me and $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$. *meso*-Tartardialdehyde, $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, and NH_2Me give a homogeneous ketone (II), m.p. 192°, reduced to two stereoisomeric alcohols one of which is identical with telodine. Hydroxytropine appears to be derived from maldialdehyde. *p*-Pelletierine is obtained directly at physiological p_H from glutardialdehyde (III), NH_2Me , and $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ with loss of CO_2 . Lobelanine is obtained in 80% yield from (III), NH_2Me , and $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{H}$ at p_H 4, the yield being dependent on p_H in an unusual degree. Examination of the probability of the synthesis of hygrine, cuskhygrine, and methylisopelletierine from suitable amino-aldehydes is hampered

by the difficulty of their prep. but the prep. of 2- β -phenylethylpyrrolidine from $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{H}$ and $\text{NH}_2\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{OEt})_2$ establishes its inherent possibility. The isoquinoline alkaloids are so complex that a complete suggestion of their biogenesis cannot yet be given, but it is shown that 6:7-dihydroxy-1-methyl-1:2:3:4-tetrahydroisoquinoline (precursor of carnegine and salsoline) is formed from a salt of β -3:4-dihydroxyphenylethylamine and MeCHO in dil. aq. solution at p_H 5. Tetrahydroharman results from tryptamine and MeCHO under physiological conditions; its further conversion into harmaline, harmalol, harmine, and harman is readily explained. Under physiological conditions the ring system of vasicine is rapidly formed from $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and $\text{NH}_2\cdot[\text{CH}_2]_3\cdot\text{CHO}$ and there is no reason to suppose that $\text{OH}\cdot\text{CH}(\text{NH}_2)\cdot[\text{CH}_2]_2\cdot\text{CHO}$ behaves differently; the peculiarity is the reversibility of the change, irreversible stabilisation being attributed to an enzyme which displaces H from positions

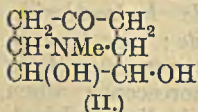


1:2 to positions 3:4. Treatment of $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ with dihydronorharman at p_H 5 gives the substance (IV) (isolated as the perchlorate), readily oxidised to rutæcarpine. From $o\text{-NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ evodiamine is derived similarly. The possibility of the existence of the supposed intermediates and their origin in the cell is critically discussed. The optical activity of the alkaloids is considered. H. W.

Lupin alkaloids. XIV. Anisylsparteine. K. WINTERFELD and E. HOFFMANN (Arch. Pharm., 1937, 275, 526–532; cf. A., 1937, II, 218).—dl-Lupanine and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$ give *p*-anisyl-dehydrosparteine, b.p. 194–202°/0.1 mm., hydrogenated very slowly to *p*-anisylsparteine (I), b.p. 188°/0.3 mm. [sulphate, $+6\text{H}_2\text{O}$, m.p. 76°; diauri-, m.p. 193° (decomp.), and platini-chloride, $+2\text{H}_2\text{O}$, decomp. 246°; picrate, m.p. 206°]. Ethyl- and phenylsparteine sulphates, phenyldehydrosparteine sulphate, and (I) have 10, 20, 10, and 30 times, respectively, the effect of sparteine sulphate (II) on the frog's heart. The effect of (II) is equal to that of methylsparteine sulphate. R. S. C.

Rotatory power of some alkaloids derived from ecgonine. C. LAPP and A. LÉVY (Bull. Sci. Pharmacol., 1937, 44, 305–325).—The alteration of $[\alpha]$ with p_H is measured for cocaine, ecgonine, benzoyle-, methyl-, and nor-ecgonine. The changes which occur as the p_H is altered are discussed in the light of their absorption spectra. J. L. D.

Alkaloid of the Chinese drug, "Kuh-Seng." II. H. KONDO, E. OCHIAI, and K. TSUDA (Arch. Pharm., 1937, 275, 493–496; cf. A., 1928, 531).—The drug contains, besides matrine, oxymatrine, $\text{C}_{15}\text{H}_{24}\text{O}_2\text{N}_2$, $+ \text{H}_2\text{O}$ (retained at 150°/vac.), m.p. 208°, $[\alpha]_D^{25} +29.8^\circ$ in EtOH , and $+x\text{H}_2\text{O}$, m.p. 77–80° (picrate, decomp. 215°; platini-, decomp. 250°, and auri-chloride, decomp. 207°; perchlorate, decomp. 240°; hydrobromide, hygroscopic, m.p. 215°; methoaurichloride, decomp. 185°; hydrochloride, hygroscopic), unaffected by $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$; the latter



base contains one *tert.* N and one CO·N. The two alkaloids are not necessarily related. R. S. C.

Aconitine. II. Relationship between aconitine and atisine and some degradation products of the latter. A. LAWSON and J. E. C. TOPPS (J.C.S., 1937, 1640—1643).—Atisine (I), $C_{22}H_{33}O_4N$, m.p. 296° (decomp.), possesses CH_2O_2 and NMe groups (cf. Jowett, J.C.S., 1896, 69, 1518; Chandrasena, A., 1933, 841). The hydrochloride of (I) is reduced (Pd-H₂) to the H₂-derivative [hydrochloride, m.p. 319° (decomp.)]. After removal of CH_2O_2 , (I) with Zn gives a base, $C_{20}H_{31}ON$ (picrate, m.p. 173°). KOEt and (I) yield a base, $C_{21}H_{31}O_2N$, m.p. 147° [hydrochloride, m.p. 278° (decomp.)], dehydrogenated (Se) to a base, b.p. 150—160°/1 mm. (picrate, m.p. 206°), and a hydrocarbon (II), $C_{17}H_{16}$. Dehydrogenation of (I) gives a base, $C_{20}H_{29}ON$, b.p. 190—200°/1 mm. [picrate, m.p. 242—243° (decomp.)]; hydrochloride, m.p. 265°, a substance, $C_{19}H_{27}O_2N$, m.p. 240°, an oil, b.p. 170—200°/1 mm., and (II), b.p. 130—160°/1 mm. (picrate, m.p. 129°; $C_6H_5(NO_2)_3$ complex, m.p. 140°). The results indicate that (I) has a pentacyclic structure and is more closely related to lucidisculine than to aconitine. F. R. S.

Dihydrokurchine. J. C. CHOWDHURY and D. H. PEACOCK (J. Indian Chem. Soc., 1937, 14, 486—488).—Kurchine (A., 1928, 1265), $C_{23}H_{38}N_2$, gives (PtO₂-H₂) dihydrokurchine [sulphate, m.p. 334° (decomp.)]; hydriodide, m.p. 222°; picrate, m.p. 176°; sulphate, m.p. 268°, of Ac derivative, m.p. 112°; NO-derivative, m.p. 109°; p-toluenesulphonyl derivative, m.p. 174°. E. W. W.

Conessine series. III. Degradation of conessine and isoconessine hydriodides to a common hydrocarbon. IV. Action of nitric acid on conessine and the reduction of one of its two isomeric mononitro-derivatives to mono-oxy- and isodioxy-conessine. S. SIDDIQUI and V. SHARMA (Proc. Indian Acad. Sci., 1937, 6, A, 191—194, 199—206).—III. Conessine (I) and isoconessine hydriodides on heating at the m.p. in H₂ give NH₃ and about 70% yield of conessene, $C_{21}H_{30}$, b.p. 185—192°/3 mm., $\alpha_D^{25} + 35.0^\circ$, which (bromination) appears to contain three double linkings.

IV. HNO₃ (1 part fuming: 1 part d 1.4) converts (I) into nitroconessine, m.p. 173°, [$\alpha_D^{25} + 11.0^\circ$ in EtOH [hydrochloride, m.p. 253° (decomp.)]; hydriodide, m.p. 252° (decomp.)]; hydrobromide, m.p. 258° (decomp.)]; platinichloride, m.p. 267° (decomp.)]; aurate, m.p. about 167°; picrate, m.p. 216°; dimethiodide, m.p. 238° (decomp.)]; dimethobromide, m.p. 237° (decomp.)], which is reduced (Zn-HCl) to a mixture of mono-oxyconessine, $C_{24}H_{40}ON_2$, m.p. 202—203°, $\alpha_D^{25} + 11.5^\circ$ [hydrochloride, m.p. 273—275° (decomp.)]; hydriodide, m.p. 352° (decomp.)]; hydrobromide, m.p. 360° (decomp.)]; platinichloride, efferv. 297°; picrate, m.p. 249° (decomp.)]; dimethiodide, m.p. 298—300° (decomp.)]; dimethobromide, m.p. 308° (decomp.)], and isodioxyconessine, $C_{24}H_{42}O_2N_2$, m.p. 279—280°, $\alpha_D^{25} - 11.0^\circ$ [hydrochloride, m.p. >360°; platinichloride, m.p. 288° (decomp.)]. With HNO₃ (3 parts fuming: 16 parts d 1.4) (I) affords isonitroconessine, $C_{24}H_{39}N_2 \cdot NO_2$, m.p. 259—260°, $\alpha_D^{25} - 45.5^\circ$ in CHCl₃ [hydrochloride (+H₂O), m.p. 239—240°

(decomp.)]; hydriodide, m.p. 295° (decomp.)]; platinichloride, m.p. 237° (decomp.)]; dimethobromide, m.p. 301° (decomp.)]. F. R. S.

Syntheses in the papaverine group. IV. **Synthesis of 6-propoxy-1-(3':4':5'-trimethoxyphenyl)-7-methoxyisoquinoline.** S. SUGASAWA and K. KAKEMI (J. Pharm. Soc. Japan, 1935, 55, 1283—1288).—*iso*Vanillin, EtOH-KOH, and PrⁿBr yield 4-methoxy-3-n-propoxybenzaldehyde, b.p. 156—158°/4 mm., m.p. 51°, which, with galloylglycine Me₃ ether, NaOAc, and AcOH, yields 2-(3':4':5'-trimethoxyphenyl)-4-(4'-methoxy-3'-n-propoxybenzylidene)-5-oxazolone, m.p. 172°. With MeOH-Na₂CO₃, this affords α -galloylamino-4-methoxy-3-n-propoxycinnamic acid Me₃ ether, m.p. 213°, which, with Cu chromite and quinoline at 160—190°, yields ω -galloylamino-4-methoxy-3-n-propoxystyrene Me₃ ether, m.p. 133°, hydrogenated to β -3-(4-methoxy-n-propoxyphenylethyl)galloylamide Me₃ ether, m.p. 109°. With PCl₅ in CHCl₃ this affords 7-methoxy-6-n-propoxy-1-(3':4':5'-trimethoxyphenyl)-3:4-dihydroisoquinoline hydrochloride, m.p. 208—209° (free base, m.p. 104°), dehydrogenated to 7-methoxy-6-n-propoxy-1-(3':4':5'-trimethoxyphenyl)isoquinoline, m.p. 208—209°. The corresponding Prⁿ compounds are prepared similarly and have b.p. 132—134°/2 mm., and m.p. 188°, 137.5°, 137.5°, 102°, 217—218°, 96—97°, and 199°, respectively. CH. ABS. (r)

Synthesis of an isomeride of domesticine ethyl ether. H. SHISHIDO (Bull. Chem. Soc. Japan, 1937, 12, 419—424).—3:4-OEt-C₆H₃(OMe)-CHO, CH₂(CO₂H)₂, and piperidine in C₅H₅N give 4-methoxy-3-ethoxycinnamic acid, m.p. 176—177.5°, reduced (H₂-Pd-C) to β -4-methoxy-3-ethoxyphenylpropionic acid, m.p. 104—106°. The amide, m.p. 123—124°, obtained from this acid by way of the chloride, with NaOEt gives β -4-methoxy-3-ethoxyphenylethylamine [oxalate, m.p. 226—227° (decomp.)]; hydrochloride, m.p. 166—168°. This affords homopiperon- β -4'-methoxy-3'-ethoxyphenylethylamide, m.p. 129—131°, converted by POCl₃ in PhMe at 130—140° into 7-methoxy-4-ethoxy-1-piperonyldihydroisoquinoline [oxalate, m.p. 227—228° (decomp.)]; the methiodide, m.p. 142—144° (decomp.), of this base gives the methochloride, which with Zn-H₂SO₄ gives 7-methoxy-4-ethoxy-1-piperonyl-1:2:3:4-tetrahydroisoquinoline, m.p. 154—154.5° [oxalate, m.p. 186—187° (decomp.)]; hydrochloride, m.p. 237—239° (decomp.)]; sulphate, m.p. 114—115° (decomp.)]. Conc. HNO₃ at <5° yields the 1-2'-nitropiperonyl compound, m.p. 128° after sintering at 123°, reduced by SnCl₂ to the 2'-NH₂-compound, m.p. 105—107° [oxalate, m.p. 186—188° (decomp.)]; hydrochloride, m.p. 220—222° (decomp.)]; sulphate, m.p. 179—181° (decomp.)], which with HNO₂-Cu-Zn-HCl gives dl-5-methoxy-6-ethoxy-2:3-methylenedioxy-N-methylaporphine, m.p. 136° [hydrobromide, m.p. 250—252° (decomp. from about 230°)], resolved by d- and l-tartaric acid into the d- and l-isomerides, m.p. 142—144°, [$\alpha_D^{25} + 90^\circ$, -90.9° in EtOH [l-base d-tartrate and d-base l-tartrate, m.p. 186—188° (decomp.)]; hydrobromide, m.p. 260—261° (decomp. from about 230°)]. The d-base depresses the m.p. of domesticine Et ether. R. S. C.

Synthetical experiments in the chelidonine-sanguinarine group of alkaloids. C. R. NOLLER, R. O. DENYES, J. W. GATES, and W. L. WASLEY (J. Amer. Chem. Soc., 1937, 59, 2079; cf. Richardson *et al.*, A., 1937, II, 356).—Various unsuccessful attempts to synthesise phenanthridines are indicated. Ring-closure of the *N*-piperonylamides of δ -piperonylisocrotonic and -propionic acid could not be accomplished. The synthesis of α -dipiperonylbutyric acid from Et piperonylmalonate and piperonylmethyl bromide is being attempted. Methylation of 2:3-(OH)₂C₆H₃CHO has been effected. H. B.

Tylophorine salts.—See A., III, 246.

Haslerine, m.p. 237°, and **quirandine**, m.p. 218°.—See A., III, 331.

Organo-arsenic compounds. VI. Synthesis of 1-chloroarsindole from cinnamic acid. VII. Synthesis of arsindole derivatives. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1937, 14, 397—399, 400—405).—VI. *o*-Aminocinnamic acid, when diazotised and treated with Na₂CO₃, H₃AsO₃, and CuSO₄, gives *tris-o*-(β -carboxyvinyl)phenylarsenic oxide, m.p. >300°, which could not be converted into an indole derivative, but the Et ester on similar treatment yields *o*-(β -carbethoxyvinyl)-, m.p. >360°, hydrolysed to *o*-(β -carboxyvinyl)-phenylarsinic acid, m.p. 205—206°. HBr in glacial AcOH converts this into β -bromohydrocinnamic-, m.p. 185°, which with aq. Na₂CO₃ affords *styrene-o*-arsinic acid, m.p. 150°. Treatment with SO₂, conc. HCl, and a little KI yields the *arsenious chloride*, m.p. 55°, cyclised by AlCl₃ in CS₂ to 1-chloroarsindole.

VII. Neither β -phenylvinylarsinic acid [from ω -bromostyrene (I) and Na arsenite] nor *Hg distyrene*, m.p. 150° [obtained, together with *Hg styryl bromide*, m.p. >330°, from (I), Na, and HgCl₂], could be converted into CHPh:CH·AsCl₂, but (I) with AsCl₃ and Na in C₆H₆-EtOAc gives *tri- β -phenylvinylarsine*, m.p. 82° (*picrate*, m.p. 100°; *methiodide*, m.p. 95°), which when heated with AsCl₃ yields 1-chloroarsindole, via the unstable dichloride. β -Phenylvinyl dimethylarsine, b.p. 125—135°/5 mm. (*methiodide*, m.p. 155°; *HgCl₂ compound*, m.p. 131°) [from (I) and AsBrMe₂, using Na in C₆H₆-EtOAc or Mg in Et₂O], was treated with Cl₂ in CCl₄ and the product heated to 190°; this gave 1-methylarsindole. With AsPhCl₂ in cold EtOH (NaOH) (I) gives a compound which when distilled yields 1-phenylarsindole. A. Li.

Aromatic aurothiol-arsenic compounds. K. BURSCHKIES (Arch. Pharm., 1937, 275, 503—506).—*p*-SH·C₆H₄·AsO₃H₂, KAUBr₂, and Na₂SO₃ give *p*-aurothiolphenylarsinic acid (Na salt). 3-Amino- (Na salt) and 3-acetamido-4-aurothiolphenylarsinic acid (Na salt) and 3:3'-diamino-4:4'-diaurothiolarsenobenzene are similarly prepared. These compounds have no therapeutic advantage over the usual anti-tuberculosis drugs. R. S. C.

Arsenobenzenesulphoxylates.—See B., 1937, 1272.

Azo-dyes and immunobiology. Destruction of anaphylactic supersensitiveness to azoprotein by azo-dyes from *p*-aminophenylarsinic acid. H. E. FIERZ, W. JADASSOHN, and W. G. STOLL (Helv. Chim.

Acta, 1937, 20, 1059—1077).—Corresponding with Pauly's assumption, azoprotein (I) whether formed *in vitro* or *in vivo* contains the ·N·N· group. The dye which destroys the anaphylactic supersensitiveness to (I) in the Schultz-Dale experiment must contain the same N₂ group as the causative (I). 4'-Sulphonyl-2'-carboxydiazoaminobenzene-4-arsinic acid (Na₂ salt, decomp. 210°), 4'-hydroxyazobenzene-4-arsinic acid, the compound, AsO(OH)₂·C₆H₄·N₂·C₆H₃(OH)·N₂·C₆H₄·AsO(OH)₂, and the dye from *p*-NH₂·C₆H₄·AsO(OH)₂ and β -C₁₀H₇·OH which exists in the quinonehydrazone (·NH·N·) and azo- (·N·N·)-forms are described. The azo-group can be fixed in the last-named compound by replacing OH by OMe, which can be effected nearly quantitatively by NaOH-Me₄SO₄. H. W.

Mercuriphenyl oleoxide and sodium ricinoleate mercuriphenyl ether.—See B., 1937, 1272.

Mercuriphenyl derivatives of aromatic acids.—See B., 1937, 1273.

Relative reactivities of organo-metallic compounds. XVII. Azo-linking. H. GILMAN and J. C. BAILIE (J. Org. Chem., 1937, 2, 84—94; cf. A., 1937, II, 359).—Organo-metallic compounds form complexes with aromatic azo-compounds, large amounts (27—77%) of Ph₂N₂ being recovered after reaction with an excess of the reagent. Ph₂N₂ gives (NHPh)₂ by symmetrical addition to form (·NPh·MgBr)₂ etc. with ZnEt₂ (31), BePh₂ (55.4), MgEtBr (58), MgPhBr (62.5), LiPh (51.8), and NaPh (25.1%); it gives NPh₂·NHPh with CaPhI (18.5) and KPh (38.4%) by asymmetric addition to form NPh₂·NPhK etc.; it gives NH₂Ph with ZnEt₂ (16), ZnEtI (12.2), ZnPh₂ (6.8), and MnPhI (53.8%) by further reaction of (NHPh)₂ with the reagent. Asymmetric addition occurs only with the most reactive reagents and the above results are confirmed by exclusive 1:2-addition of the reactive CaPhI and KPh and partial 1:2-addition of LiPh and NaPh to ·CH:CH·CO·. Reaction of organo-Al compounds is accompanied by condensation and polymerisation. The mechanism of various apparently abnormal Grignard additions is discussed. R. S. C.

Reduction of lead organic nitro-compounds. K. A. KOTSCHESCHKOV and G. M. BORODINA (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1937, 569—576).—PbPh₂(NO₂)₂ and fuming HNO₃ (7 hr. at 100°) yield [m-C₆H₄(NO₂)₂]₂Pb(NO₃)₂, converted by HBr into *Pb di-m-nitrophenyl dibromide*, reduction of which in acid, alkaline, or neutral solution leads to formation of amine, which immediately decomposes into NH₂Ph and PbBr₂. R. T.

Polarity of the co-ordinate link. II. Influence of aromatic substitution on the stability of the phosphinimines. F. G. MANN and E. J. CHAPLIN (J.C.S., 1937, 527—535).—The action of chloramine-*T* (I) on *tert.* phosphines (cf. A., 1932, 528) has now been investigated, each phosphine having been treated (a) with the anhyd. reagent in abs. alcoholic solution, and (b) with the hydrated reagent in rectified spirit. Under conditions (a), only a true phosphinimine, R₃P→N·SO₂·C₆H₄Me, was

formed, whereas under (b) a phosphinimine or the hydroxyphosphinesulphonamide, $\text{OH}\cdot\text{PR}_3\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, could be obtained according to the strength of the polarity of the co-ordinate link in the initial phosphinimine. PPh_3 and (I) give (a) *triphenylphosphine-p-toluenesulphonylimine*, m.p. 187°, and (b) *NN-bis-(p-toluenesulphonamido-triphenylphosphine)-p-toluenesulphonamide*, m.p. 138°. *Tri-o-tolylphosphine*, m.p. 125°, obtained from PCl_3 and $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{HgBr}$, with (I) affords (a) *tri-o-tolylphosphine-p-toluenesulphonylimine*, m.p. 188°, and (b) the phosphinimine and *tri-o-tolylphosphine oxide* ($+0.5\text{H}_2\text{O}$), m.p. 153°. $\text{P}(\text{C}_6\text{H}_4\text{Me-p})_3$ and (I) yield (a) *tri-p-tolylphosphine-p-toluenesulphonylimine*, m.p. 174°, and (b) the phosphinimine and *hydroxytri-p-tolylphosphine-p-toluenesulphonamide*, m.p. 106°. *Tri-m-tolylphosphine*, m.p. 100°, with (I) forms (a) a syrup, from which a well-defined phosphinimine cannot be obtained and (b) *hydroxytri-m-tolylphosphine-p-toluenesulphonamide*, m.p. 98°, also obtained from *tri-m-tolylphosphine oxide*, m.p. 111°, and $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ (II). *Tri-o-anisylphosphine*, m.p. 204°, prepared from PCl_3 and $\text{o-C}_6\text{H}_4\text{Br}\cdot\text{OMe}$, with (I) gives (a) *tri-o-anisylphosphine-p-toluenesulphonylimine*, m.p. 273—274°, and (b) the phosphinimine and *hydroxytri-o-anisylphosphine-p-toluenesulphonamide*, m.p. 149°. *Tribromotri-o-anisylphosphine oxide*, m.p. 245°, is obtained by bromination of the phosphine, followed by alkaline hydrolysis. *Tri-p-anisylphosphine*, m.p. 131°, and (I) afford (a) *tri-p-anisylphosphine-p-toluenesulphonylimine*, m.p. 155°, and (b) *hydroxytri-p-anisylphosphine-p-toluenesulphonamide*, m.p. 121°, only. *Tri-m-anisylphosphine*, m.p. 115°, and (I) yield (a) a glass and (b) *hydroxytri-m-anisylphosphine-p-toluenesulphonamide*, m.p. 112°, easily converted into *tri-m-anisylphosphine oxide*, m.p. 151—152°, and (II). *Tri-o-chlorophenylphosphine*, m.p. 185°, prepared from $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{MgI}$ and PCl_3 in H_2 , and (I) give (a) *tri-o-chlorophenylphosphine-p-toluenesulphonylimine*, m.p. 235—236°, and (b) the phosphinimine and no hydroxy-sulphonamide, which could not be obtained from *tri-o-chlorophenylphosphine oxide* ($+0.5\text{H}_2\text{O}$), m.p. 226—236°. *Tri-p-chlorophenylphosphine*, m.p. 103°, with (I) yields (a) *tri-p-chlorophenylphosphine-p-toluenesulphonylimine*, m.p. 232°, and (b) *tri-p-chlorophenylphosphine oxide*, m.p. 175°, and (II). *Tri-m-chlorophenylphosphine*, m.p. 67°, with (I) affords (a) and (b) $\text{PO}(\text{C}_6\text{H}_4\text{Cl-m})_3$. PPhMe_2 and (I) do not give a cryst. product, whilst PPhEt_2 affords (a) and (b) *phenyldiethylphosphine-p-toluenesulphonylimine*, m.p. 82°. $\text{PEt}_2\cdot\text{C}_6\text{H}_4\text{Me-p}$ and (I) yield (a) and (b) *p-tolyldiethylphosphine-p-toluenesulphonylimine*, m.p. 120°, and similarly obtained are *triethyl-*, m.p. 119°, *tri-n-propyl-*, m.p. 66°, and *tri-n-butylphosphine-p-toluenesulphonylimine*, m.p. 54°. *Triphenyl-*, m.p. 192—193°, *tri-o-*, m.p. 201—202°, and *tri-p-tolyl-arsine-p-toluenesulphonylimine*, m.p. 185°, are obtained from (I) and the corresponding arsine under conditions (a). The results are dependent on the fact that Me, OMe, and Cl are *op*-directing, and the theoretical significance is discussed.

F. R. S.

Magnetochemical investigations of organic compounds. XII. Potassium benzil and potass-

ium phenanthraquinone. E. MÜLLER and W. WIESEMANN (Annalen, 1937, 532, 116—126).—The product of the interaction of molar proportions of benzil (I) and K, Ph diphenyl ketone (II), is converted by BzBr into (I) and $(\text{CPh}\cdot\text{OBz})_2$. It is transformed by protracted agitation with Ph_2S_2 into (I) and PhSH which is oxidised to Ph_2S_2 . It is hydrolysed to (I) and $\text{OH}\cdot\text{CHPh}\cdot\text{Bz}$. Gradual addition of increasing amounts of (I) to (II) (cf. Schlenk, A., 1913, i, 1205) and determination of the magnetic susceptibility of the product shows that free K benzil exists, but all materials previously mistaken for it are mixtures of it with (I) and K stilbenediol (II), in which (I) and (II) are united to a quinhedrone compound. Under the experimental conditions its prep. in the pure state is practically impossible and its existence as solid is very doubtful. Similarly, the material regarded as K phenanthraquinone is a mixture of this substance with phenanthraquinone and K phenanthraquinol. The so-called K xanthone and K benzanthrone are similar mixtures of compounds. The relative solubilities of the different components appear to determine the composition of the ppts. In the present instances definite mol. relationships between the quinhedrone or its constituents and the radical do not exist.

H. W.

Reaction between proteins and metaphosphoric acid. H. HERRMANN and G. PERLMANN (Nature, 1937, 140, 807).—Analytical data obtained with the ppts. formed from egg-albumin (I) or clupein sulphate (II) and HPO_3 are recorded. The amount of P bound agrees with the no. of free NH_2 in (I) or with the no. of positively charged NH_2 in (II).

L. S. T.

Simplified quantitative hydrogenation of milligrams and centigrams of substances. C. WEYGAND and A. WERNER (J. pr. Chem., 1937, [ii], 149, 330—336).—A simplified apparatus for rapidly and quantitatively hydrogenating (PtO_2) 3—5 or 30—50 mg. of substances is described. Errors in the hydrogenation of 10 substances with 1—9 ethylenic linkings were 0—1.6%.

R. S. C.

Determination of alkyl- and aryl-halogen in presence of each other. W. H. RAUSCHER (Ind. Eng. Chem. [Anal.], 1937, 9, 503—504; cf. A., 1937, II, 358).—The author's method gives results having errors <0.1%.

F. R. G.

Micro-determination of organic sulphur. W. SASCHER (Ind. Eng. Chem. [Anal.], 1937, 9, 491—492).—A modification of Pregl's method. The combustion tube is washed out with 1 in 300 HCl into a crucible in which BaSO_4 is pptd. and the liquid removed by suction through a filter stick. Transference of ppt. is thus avoided.

F. R. G.

Qualitative organic analysis. Identification of alkyl halides, amines, and acids. (Miss) E. L. BROWN and N. CAMPBELL (J.C.S., 1937, 1699—1701).—Primary and sec. alkyl bromides and iodides are identified by the formation with $\text{CS}(\text{NH}_2)_2$ of *S*-alkylisothiocarbamides; the following are described: *n*-, m.p. 181°, and *iso-propyl*-, m.p. 148°, *n*-, m.p. 180°, *iso*-, m.p. 174°, and *sec.-butyl*-, m.p. 190°.

n-, m.p. 154°, iso-, m.p. 179°, and sec.-*amyl*-, m.p. 143°, n-*hexyl*-, m.p. 157°, and benzyl-isothiocarbamide picrate, m.p. 188°. $(\text{CH}_2\text{Br})_2$ yields ethylene bis(isothiocarbamide) (picrate, m.p. 270°). pp'-Diphenylthiocarbamide, m.p. 233—235° (from $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$, CS_2 , $\text{C}_5\text{H}_5\text{N}$, and I), is converted by Ac_2O into 4-diphenylthiocarbimide (I), m.p. 70°. Aliphatic amines are identified by interaction with (I) or with β -naphthylthiocarbimide, and the following are described, the m.p. recorded being those of the N-alkyl- (or -diakyl)-N'-4-diphenylthiocarbamide, and the N-alkyl (or dialkyl)-N'- β -naphthylthiocarbamide, respectively: methyl- (142°, 127°), ethyl- (165°, 142°), n-propyl- (156°, 114°), n- (155°, 119°) and iso-butyl (157°, 137°), n- (147°, 114°) and iso-*amyl*-, (130°, 116°), n-heptyl (149°, 115°), dimethyl- (225°, 173°), diethyl- (114°, 90°), dipropyl- (117°, 109°), diisobutyl- (160°, 136°), di-n-*amyl*- (118°, 126°), benzyl- (147°, 173°), cyclohexyl- (180°, 172°), bornyl- (167°, —), camphyl- (138°, 127°), and ethylenebis- (237° 223°). 2:4:5- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ with the appropriate primary amine yields N-ethyl-, m.p. 126°, -n-propyl-, m.p. 101°, -n-, m.p. 96°, and -iso-butyl-, m.p. 112°, -n-, m.p. 99°, and -iso-*amyl*-, m.p. 82°, -n-heptyl, m.p. 50°, and -benzyl-4:6-dinitro-m-toluidine. $(\text{CH}_2\cdot\text{NH}_2)_2$ yields NN'-bis-(2:4-dinitro-5-methylphenyl)ethylene-diamine, m.p. 280°. Org. acids are identified by formation of the 2-alkylbenziminazole with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, and the following are described: 2-methyl-, m.p. 214°, -ethyl-, m.p. 120°, -n-, m.p. 124°, and -iso-propyl-, m.p. 136°, -*amyl*-, m.p. 282°, -hydroxy-ethyl-, m.p. 131°, -hydroxymethyl-, m.p. 214°, and -phenylhydroxymethyl-benziminazole picrate, m.p. 209°. Alkyl nitrites are identified by formation of 3-oximino-2-phenylindole with 2-phenylindole. An improved prep. of 2:4-dinitrobenzoic acid is described.

J. D. R.

Determination of glycol or glycerol in dilute solutions containing oxidisable impurities. W. E. SHAEFER (Ind. Eng. Chem. [Anal.], 1937, 9, 449—450).—50 c.c. of solution containing <2.5 g. of $(\text{CH}_2\cdot\text{OH})_2$ and free from mol. compounds are neutralised and distilled with a three-bulb Snyder column to 10 c.c.; 50 c.c. of dry $\text{C}_5\text{H}_5\text{N}$ are added and the mixture is distilled to 110°, the residue being acetylated with 25 c.c. of 2:6-N- Ac_2O in $\text{C}_5\text{H}_5\text{N}$, then diluted, and titrated, while shaking, with N-NaOH. The result is compared with a blank val. The method can be used for glycerol, and after applying a correction the accuracy is 1%.

F. R. G.

Determination of β -butylene glycol. Y. TOMIYASU (J. Agric. Chem. Soc. Japan, 1937, 13, 972—977).—Acetoin is first removed from the liquid by distillation (cf. A., 1937, II, 443). The residue is heated with Br and NaOAc, the excess of Br exactly removed by $\text{Na}_2\text{S}_2\text{O}_3$, and then the liquid is distilled into aq. NiCl_2 solution. Wt. of ppt. $\times 0.88 = \beta$ -butylene glycol.

J. N. A.

Volumetric determination of polyhydric alcohols and reducing aldoses (monosaccharides) by means of periodate, and the determination of periodate and iodate in presence of each other. I. F. RAPPAPORT, I. REIFER, and H. WEINMANN

(Mikrochim. Acta, 1937, 1, 290—299).—I set free at p_{H} 4.4—7 from solutions of KIO_3 and KIO_4 in presence of KI corresponds with the KIO_4 present. Glucose (I), mannitol (II), and sorbitol (III) can be determined in acid or alkaline solution by means of the periodate method. (II) and (III) can be determined in presence of (I) by determining (I) by means of Fujita and Iwatake's method and the total sugar by means of periodate. Galactose and its admixture with (II) and (III) can similarly be determined but only in acid solution.

C. R. H.

Quantitative acetylation of amines by acetyl chloride and pyridine. V. R. OLSON and H. B. FELDMAN (J. Amer. Chem. Soc., 1937, 59, 2003—2005).—Smith and Bryant's method (A., 1935, 369) of determination of OH, which gives inconsistent results with amines and amides, is modified. Using $\text{AcCl} + \text{C}_5\text{H}_5\text{N}$ in Bu_2O at 70° and compounds which are sol. in the reagent, vals. >90% of the theoretical are generally obtained.

H. B.

Effect of aldehydes on cystine and cysteine. W. C. HESS and M. X. SULLIVAN (J. Biol. Chem., 1937, 121, 323—329).—Through formation of complexes, aldehydes have a marked effect on the determination of cystine by the Sullivan method, the effect increasing with decreasing acidity, with increasing concn. of the reactants, and with increase in the val. of the ratio aldehyde:cystine. Aldehydes do not affect the determination of cystine either in dil. or in conc. solutions.

C. R. H.

Detection of thiocarbamide. E. STORFER (Mikrochim. Acta, 1937, 1, 260—263).—The substance to be tested is gently heated for 2—4 min. with H_2O , mixed with dry CuCl_2 or other Cu salt, boiled for 1 min., and filtered. A drop of the filtrate, which must be neutral, is brought on to filter-paper soaked in $\text{K}_3\text{Fe}(\text{CN})_6$. A violet-blue colour indicates the presence of $\text{CS}(\text{NH}_2)_2$. $\text{EtOH-H}_2\text{O}$ and $\text{COMe}_2\text{-H}_2\text{O}$ solutions sometimes give better results. High-mol. products, e.g., resins, must first be decomposed by treatment with syrupy H_3PO_4 at 100—150° followed by neutralisation with NaOH. 0.00001 g. of $\text{CS}(\text{NH}_2)_2$ can be detected.

C. R. H.

Micro-method for measuring rate of decomposition of diazoacetic esters. P. GROSS, H. STEINER, and F. KRAUSS (Mikrochim. Acta, 1937, 1, 87—91).—A micro-gas volumeter is described.

J. S. A.

Quinone reactions. G. WOKER and U. ANTENER (Helv. Chim. Acta, 1937, 20, 1260—1270).—The complication in the detection of ascorbic acid caused by the development of colour by benzoquinone (I) and tissue only (A., 1937, II, 367) is not attributable to $\text{C}_6\text{H}_4\cdot\text{OH}$, carbohydrate group, or readily eliminated S but is given by the isolated NH_2 -acids. This explanation is quantitatively inadequate; in the reaction of (I) and proteins the effect is due to the NH_2 -acids, particularly histidine, lysine, arginine, ornithine, and proline, and also to NH_3 obtained by their deamination. The possible structures of the compounds thus formed are discussed. Similar reactions are afforded by triketohydrindene (cf. Cherbuliez, A., 1935, 102).

H. W.